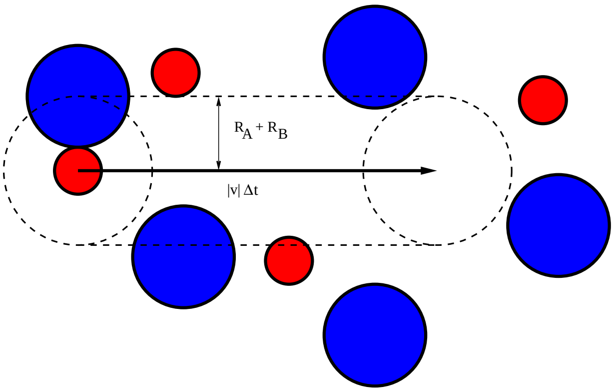
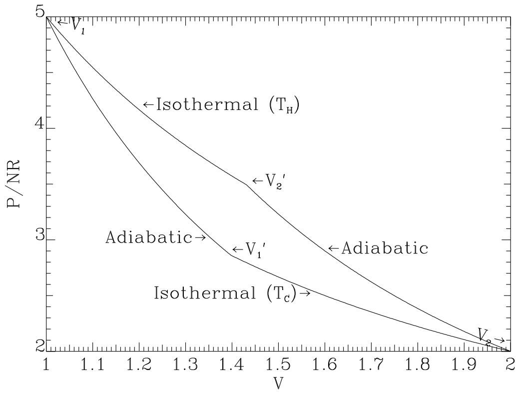


Chemistry 223: Introductory Physical Chemistry I

David Ronis

McGill University



Chemistry 223

Introductory Physical

Chemistry I

David Ronis

McGill University

All truths are easy to understand once they are discovered; the point is to discover them.

Philosophy is written in this grand book-I mean the universe-which stands continually open to our gaze, but it cannot be understood unless one first learns to comprehend the language and interpret the characters in which it is written. It is written in the language of mathematics, and its characters are triangles, circles, and other geometrical figures, without which it is humanly impossible to understand a single word of it.

Opere Il Saggiatore
Galileo Galilei (1564 - 1642)

A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that within the framework of the applicability of its basic concepts, it will never be overthrown.

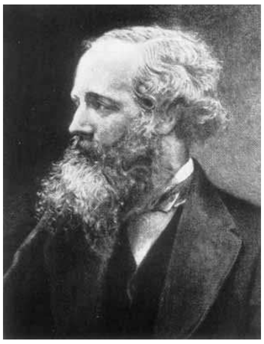
Albert Einstein (1879 - 1955)

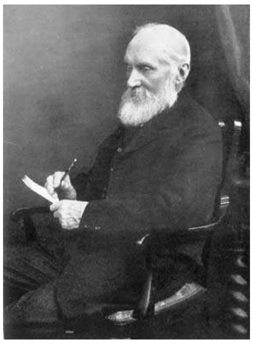
The Founders of Thermodynamics and the Kinetic Theory of Gases

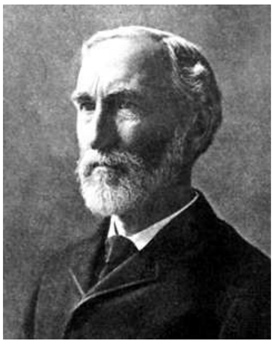

Joule


Carnot


Clausius


Maxwell


Kelvin


Gibbs


Boltzmann

Fall Term, 2015

Table of Contents

1. General Information . . . 3
1.1. Contact Information . . . 3
1.2. Texts . . . 4
1.3. Supplementary Texts . . . 4
1.4. Grades . . . 4
1.5. Random, McGill Specific, Notes . . . 5
1.6. Tentative Course Outline . . . 6
2. *Divertissements* . . . 7
2.1. *Divertissement* 1: Founders of the first law of thermodynamics . . . 7
2.2. *Divertissement* 2: Why do we have winter heating? . . . 7
2.3. *Divertissement* 3: Nicolas Leonard Sadi Carnot . . . 9
2.4. *Divertissement* 4: Absolute Temperature . . . 9
2.5. *Divertissement* 8: On the names of thermodynamic functions . . . 10
3. Some Properties of Ideal and Non-Ideal Materials . . . 12
3.1. Ideal Gases . . . 12
3.2. Dalton's Law . . . 12
3.3. Beyond Ideal Gases . . . 13
3.4. Liquids and Solids . . . 19
4. Probability and Statistics . . . 21
5. Maxwell-Boltzmann Distribution . . . 24
5.1. Appendix: Proof of Equation (5.4) . . . 29
6. Collisions, Reactions, and Transport . . . 31
6.1. Effusion, Surface Collisions and Reactions . . . 31
6.2. Gas Phase Collisions and Chemical Reactions . . . 31
6.3. Mean Free Path and Transport Phenomena . . . 34
6.4. Appendix: The Center of Mass Frame . . . 37
7. Work, Heat, and Energy . . . 39
7.1. Zeroth Law of Thermodynamics . . . 39
7.2. Some Definitions . . . 39
7.3. Euler's Theorem, Partial Molar Quantities, . . . 41
7.4. Work and Heat in Thermodynamics . . . 42
7.5. The First Law of Thermodynamics: . . . 45
7.7. Appendix: Energy in Classical Mechanics . . . 47
8. Thermochemistry . . . 50
8.1. Enthalpy Calculations: Chemical Reactions and Hess' Law . . . 50
8.2. Measuring ΔH_f^0 . . . 51
8.3. Reactions at Different Temperatures: Kirchoff's Law . . . 52
8.4. Bond Energies . . . 53
8.5. Some Manipulations Involving Thermodynamic Functions . . . 55
8.5.1. The relationship between C_P and C_V . . . 55
8.5.2. The Joule-Thompson Experiment . . . 56
9. Ideal Gas Carnot Engines and Efficiency . . . 59
9.1. Energy in an Ideal Gas: Joule's Experiment . . . 59

9.2. Reversible, Adiabatic Expansion or Compression of an Ideal Gas 61
9.3. Reversible, Isothermal Expansion or Compression of an Ideal Gas 61
9.4. Entropy Changes in the Ideal Gas Carnot Cycle 62
10. Ideal Gas Carnot Engines and Efficiency 64
10.1. Efficiency of Real Carnot Engines 67
10.2. The Clausius Inequality and the Second Law 71
10.3. Entropy Calculations 73
11. The Third Law of Thermodynamics 75
12. The Chemical Potential 77
13. State Functions, Exact Differentials, and Maxwell Relations 79
13.1. Applications to Thermodynamics: Maxwell Relations 80
13.2. Maxwell Relations: A Complicated Example 80
13.3. Appendix: Proof of Green's Theorem in the Plane 82
14. Thermodynamic Stability: Free Energy and Chemical Equilibrium . . 85
14.1. Spontaneity and Stability Under Various Conditions 85
14.2. Examples of free energy calculations 89
14.2.1. Coupled Reactions 90
14.2.2. General Trends 90
14.3. Chemical Equilibrium 92
14.3.1. Thermodynamics of Chemically Reacting Systems 92
14.4.1. Chemical Potentials in Pure Materials 94
14.4.2. Chemical Potentials in Ideal Gas Mixtures 95
14.5.1. Determination of Free Energies of Formation 96
14.5.2. Determination of the Extent of a Reaction 97
14.5.3. Temperature Dependence of K_P 97
14.5.4. Free Energy and Entropy of Mixing 98
15. Thermodynamic Stability 100
16. Entropy & Randomness 104
17. Electrochemical Cells 107
17.1. General Considerations 107
17.2. Concentration Cells 109
17.3. Connection to Equilibrium Constants 110
17.4. Temperature effects 110
18. Problem Sets 111
18.1. Problem Set 1 111
18.2. Problem Set 2 112
18.3. Problem Set 3 114
18.4. Problem Set 4 116
18.5. Problem Set 5 117
18.6. Problem Set 6 119
19. Past Midterm Exams 122
19.1. 2012 Midterm Exam 122
19.2. 2013 Midterm Exam. 125
19.3. 2014 Midterm Exam 128
19.4. 2015 Midterm Exam 131
20. Past Final Exams 134
20.1. 2012 Final Exam 134

1. General Information

CHEMISTRY 223: Introductory Physical Chemistry I.

Kinetics 1: Gas laws, kinetic theory of collisions. Thermodynamics: Zeroth law of thermodynamics. First law of thermodynamics, heat capacity, enthalpy, thermochemistry, bond energies. Second law of thermodynamics; the entropy and free energy functions. Third law of thermodynamics, absolute entropies, free energies, Maxwell relations and chemical and thermodynamic equilibrium states.

Prerequisites: CHEM 110, CHEM 120 or equivalent, PHYS 142, or permission of instructor.
Corequisite: MATH 222 or equivalent.
Restrictions: Not open to students who have taken or are taking CHEM 203 or CHEM 204.

1.1. Contact Information

Professor:	David Ronis
Office:	Otto Maass 426
E-mail:	David.Ronis@McGill.CA (Help my e-mail client direct your email; Please put CHEM 223 somewhere in the subject.)
Tutor/Grader:	Samuel Palato
E-mail:	Samuel.Palato@Mail.McGill.CA
Office:	Otto Maass 25
Lectures:	Tuesday and Thursday 11:35 - 12:25
Makeups, Tutorials, or Review Sessions:	Friday 11:35 - 12:25
Location:	Otto Maass 217
Course Web Site:	https://ronispc.chem.mcgill.ca/ronis/chem223 Note: username and password are needed for full access.

I will be away on the following dates and will make up the missed class in the Friday slot of the same week:

Canceled Classes (Fall, 2015)	Makeup (OM 217, 11:35-12:25)
Tuesday, September 15	Friday, September 18
Tuesday, September 29	Friday, October 2
Tuesday, October 6	Friday, October 9

1.2. Texts

Thomas Engel and Philip Reid, *Thermodynamics, Statistical Thermodynamics, and Kinetics, 3rd edition* (Pearson Education, Inc., 2013).

J.R. Barrante, *Applied Mathematics for Physical Chemistry, 3rd edition* (Pearson Education, Inc., 2004).

1.3. Supplementary Texts

1. G. W. Castellan, *Physical Chemistry* 3rd edition (Benjamin Cummings Pub. Co., 1983) (Out of print but excellent. This would be the text for the course if I could get copies). Note that Castellan doesn't use SI units and uses a older sign convention for an key-- thermodynamic quantity, namely work.
2. R.J. Silbey, R.A. Alberty and M.G. Bawendi, *Physical Chemistry, 4th edition* (John Wiley & Sons, Inc., 2005). This was used as the text in the past. It's OK but Engel and Reid or Castellan are better.
3. R. Kubo, *Thermodynamics* (Physics orientation, excellent, but somewhat advanced with fewer chemical examples).

1.4. Grades

There will be approximately one problem set every 2-3 lectures, one midterm and a final exam. The midterm will be given between 6 and 9 P.M. on

Tuesday, October 27, 2015
in Otto Maass 112 and 217 (a seating plan will be posted).

Completion and submission of the homework is mandatory. We have a tutor/grader for the course, Samuel Palato, and the problems will be graded. Solutions to the problem sets will be posted on the course web page. In addition, there will be a tutorial roughly every second Friday where the tutor will go over problems or review other topics.

You are strongly encouraged to do the homework by yourself. The problems will cover many details not done in class and will prepare you for the exams. **The exams will involve extensive problem solving and may contain problems from the homework!** The course grading scheme is:

Grade Distribution	
Problems	10%
Midterm	40%
Final	50%

1.5. Random, McGill Specific, Notes

McGill University values academic integrity. Therefore, all students must understand the meaning and consequences of cheating, plagiarism and other academic offenses under the Code of Student Conduct and Disciplinary Procedures (see www.mcgill.ca/students/srr/honest/ for more information).(approved by Senate on 29 January 2003)

In accord with McGill University's Charter of Students' Rights, students in this course have the right to submit in English or in French any written work that is to be graded. (approved by Senate on 21 January 2009)

In the event of extraordinary circumstances beyond the University's control, the content and/or evaluation scheme in this course is subject to change.

1.6. Tentative Course Outline

Lecture	Topic	Text Chapter		
		Silbey	Reid	Castellan
Lecture 1.	Introduction: Kinetics & Thermodynamics, an overview	1	1	2
Lecture 2.	Empirical properties of gases	1	1,7	2
Lecture 3.	Empirical properties of liquids and solids	1	1	5
Lecture 4.	Molecular basis: Kinetic theory of gases	17	12, 16	4
Lecture 5.	Surface reactions & Effusion	17	16	30
Lecture 6.	Gas phase collision rates	17	16	30
Lecture 7.	Kinetics I: Collision theory of elementary gas phase reactions: Collision rates and activation energies	19	17	33
Lecture 8.	Mean free path & Diffusion			
Lecture 9.	Kinetics I: Review of n'th order reaction kinetics.	18	18	32
Lecture 10.	Intro. to mechanims & steady state approximation.			
Lecture 11.	Temperature: the zeroth law of thermodynamics	1	1	6
Lecture 12.	Mechanics, Work, and Heat	2	2	7
Lecture 13.	Reversible and irreversible changes	2	2	7
Lecture 14.	The First Law of Thermodynamics: Energy	2	2, 3	7
Lecture 15.	Enthalpy, Hess's Law	2	3, 4	7
Lecture 16.	Heat Capacities, Kirchoff's Law	2	4	7
Lecture 17.	Estimating Enthalpy Changes: Bond Enthalpies	2	4	7
Lecture 18.	The Carnot Engine/Refrigerator	3	5	8
Lecture 19.	The Second Law of Thermodynamics: Entropy	3	5	8
Lecture 20.	Entropy Calculations	3	5	8
Lecture 21.	The Third Law of Thermodynamics: Absolute Entropies	3	5	9
Lecture 22.	Conditions for Stable Equilibrium: Free Energies	4	6	10
Lecture 23.	Equilibrium Conditions (continued)	4	6	10
Lecture 24.	Maxwell Relations and applications	4	6	9.4
Lecture 25.	Chemical equilibrium	5	6	11
Lecture 26.	Chemical equilibrium calculations	5	6	11

2. *Divertissements*

From: Ryogo Kubo, *Thermodynamics* (North Holland, 1976)

2.1. *Divertissement* 1: Founders of the first law of thermodynamics

If a tomb of the Unknown Scientists had been built in the 1850's, the most appropriate inscription would have been "In memory of the grief and sacrifice of those who fought to realize a perpetuum mobile". But the law of conservation of energy, or the first law of thermodynamics, is associated primarily with three great names, Mayer, Helmholtz and Joule.

Julius Robert Mayer (1814-1878) was really a genius who was born in this world only with the errand to make this great declaration. Hermann Ludwig Ferdinand von Helmholtz (1821-1894) gave this law the name "Erhaltung der Kraft" or "the conservation of energy". Like Mayer, he started his career as a medical doctor but lived a glorious life as the greatest physiologist and physicist of the day. James Prescott Joule (1818-1889) worked over forty years to establish the experimental verification of the equivalence of work and heat.

Among the three, Mayer was the first who arrived at this law and the last whose work was recognized. His life was most dramatic. A lightening stroke of genius overtook him, a German doctor of the age of twenty six, one day on the sea near Java when he noticed that venous blood of a patient under surgical operation appeared an unusually fresh red. He considered that this might be connected with Lavoisier's theory of oxidation in animals, which process becomes slower in tropical zones because the rate of heat loss by animals will be slower there. A great generalization of this observation lead him to the idea of the equivalence of heat and mechanical work. For three years after his voyage, while he was working as a medical doctor at home, he devoted himself to complete the first work on the conservation of energy "Bemerkungen uber die Krafte der unbelebten Natur" which was sent to the Poggendorf Annalen and was never published by it. In 1842 Liebig published this paper in his journal (Annalen der Chemie und Pharmacie) but it was ignored for many years.

Mayer wrote four papers before 1851. During these years of unusual activity he cared for nothing other than his theory. In 1852 he became mentally deranged and was hospitalized. He recovered after two years but never returned to science.

2.2. *Divertissement* 2: Why do we have winter heating?

Why do we have winter heating? The layman will answer: "To make the room warmer." The student of thermodynamics will perhaps so express it: "To import the lacking (inner, thermal) energy." If so, then the layman's answer is right, the scientist's is wrong.

We suppose, to correspond to the actual state of affairs, that the pressure of the air in the room always equals that of the external air. In the usual notation, the (inner, thermal) energy is, per unit mass,*

$$u = c_v T .$$

*The author has assumed that the specific heat of the gas is independent of temperature; a reasonable approximation for the oxygen and nitrogen around room temperature.

(An additive constant may be neglected.) Then the energy content is, per unit of volume,

$$u = c_v \rho T,$$

or, taking into account the equation of state, we have

$$\frac{P}{\rho} = RT,$$

we have

$$u = c_v P/R.$$

For air at atmospheric pressure,

$$u = 0.0604 cal/cm^3.$$

The energy content of the room is thus independent of the temperature, solely determined by the state of the barometer. The whole of the energy imported by the heating escapes through the pores of the walls of the room to the outside air.

I fetch a bottle of claret from the cold cellar and put it to be tempered in the warm room. It becomes warmer, but the increased energy content is not borrowed from the air of the room but is brought in from outside. Then why do we have heating? For the same reason that life on the earth needs the radiation of the sun. But this does not exist on the incident energy, for the latter apart from a negligible amount is re-radiated, just as a man, in spite of continual absorption of nourishment, maintains a constant body-weight. Our conditions of existence require a determinate degree of temperature, and for the maintenance of this there is needed not addition of energy but addition of entropy.

As a student, I read with advantage a small book by F. Wald entitled "The Mistress of the World and her Shadow". These meant energy and entropy. In the course of advancing knowledge the two seem to me to have exchanged places. In the huge manufactory of natural processes, the principle of entropy occupies the position of manager, for it dictates the manner and method of the whole business, whilst the principle of energy merely does the bookkeeping, balancing credits and debits.

R. EMDEN

Kempterstrasse 5,
Zurich.

The above is a note published in Nature **141** (l938) 908. A. Sommerfeld found it so interesting that he cited it in his book *Thermodynamic und Statistik* (Vorlesungen uber theoretische Physik, Bd. 5, Dietrich'sche Verlag, Wiesbaden; English translation by F. Kestin, Academic Press Tic., New York, 1956). R. Emden is known by his work in astrophysics and meteorology as represented by an article in der Enzyklopadie der mathematischen Wissenschafte *Thermodynamik der Himmelskorper* (Teubuer, Leipzig-Berlin, 1926).

2.3. *Divertissement* 3: Nicolas Leonard Sadi Carnot

In the first half of the last century, the steam engine, completed by introduction of the condenser (the low-temperature heat reservoir), due to James Watt (1765) had come to produce more and more revolutionary effects on developments in industry and transportation. Many eminent physicists like Laplace and Poisson set about to study the Motive Power of Fire. Sadi Carnot (1796-1832) was a son of Lazare Carnot, Organizer of Victory in the French Revolution, and was born and died in Paris. He probably learned the caloric theory of heat, in which heat was assumed to be a substance capable either of flowing from body to body (heat conduction) or of making chemical compound with atoms (latent heat). He wrote a short but very important book, *Reflexions sur la puissance motrice du feu et sur les machines propres a developper cette puissance* (Paris, 1824), which was reprinted by his brother (1878) together with some of Carnot's posthumous manuscripts.

Carnot directed his attention to the point that, in the heat engine, work was done not at the expense of heat but in connection with the transfer of heat from a hot body to a cold body, and thus heat could not be used without a cold body, in analogy of water falling from a high reservoir to a low reservoir. In his book he assumed the law of conversation of heat, namely that the quantity of heat was a state function, although he later abandoned this law and arrived at the law of equivalence of heat and work: he actually proposed many methods to estimate the mechanical equivalent of heat. He introduced what came to be known as Carnot's cycle, and established Carnot's principle.

Carnot's book had been overlooked until B. P. E. Clapeyron (1834) gave Carnot's theory an analytical and graphical expression by making use of the indicator diagram devised by Watt. The law of conservation of heat assumed by Carnot was corrected by R. Clausius (1850), based on the work of J. R. von Mayer (1841) and J. P. Joule (1843-49), into the form that not only a change in the distribution of heat but also a consumption of heat proportional to the work done is necessary to do work, and vice versa. Clausius named this modification the First Law of Thermodynamics. H. L. F. van Helmholtz (1847) and Clausius generalized this law to the principle of the conservation of energy. W. Thomson (Lord Kelvin), who introduced Kelvin's scale of temperature (1848) based on Carnot's work, also recognized the law of equivalence of heat and work. The Second Law of Thermodynamics was formulated by Thomson (1851) and Clausius (1867).

A sketch of the history of early thermodynamics is given by E. Mendoza, Physics Today 14 (1961) No. 2, p. 32. See also E. Mach: *Principien der Warmelehre* (vierte Aufl. 1923, Verlag von Johann Ambrosius Barth, Leipzig).

2.4. *Divertissement* 4: Absolute Temperature

The absolute temperature scale means that temperature scale which is determined by a thermodynamic method so that it does not depend on the choice of thermometric substance, the zero of the scale being defined as the lowest temperature which is possible thermodynamically. Absolute temperature, which is now used in thermal physics, was introduced by Lord Kelvin (William Thomson) in 1848 and is also called the Kelvin temperature.

For the complete definition of the scale, we have two choices; one is to use two fixed points above zero and assign their temperature difference and the other is to use one fixed point and assign its numerical value. Until recently the calibration of the Kelvin temperature scale was performed using two fixed points: the ice point $T_0{}^oK$ and the boiling point $T_0 + 100^oK$ of pure water under 1 standard atm (= 101325 Pa). We can measure T_0 by a gas thermometric method. At low pressures, the equation of state of a real gas can be written in the form

$$pV = \alpha + \kappa p.$$

We measure the values of pV, α and κ at the above two fixed points.Considering that α is equal to nRT, we have

$$T_0 = \frac{100\alpha_0}{\alpha_{100} - \alpha_0}$$

If we put $T_0 = 0$, we get the thermodynamic Celsius temperature scale. Hence, $-T_0{}^oC$ means absolute zero as measured by this scale.

The precise gas thermometric investigations of the Frenchman P. Chappuis from 1887 to 1917 gave the value of T_0 between 273.048 and 273.123. Inspired by this work, more than one hundred determinations of T_0 were performed until 1942. Among them, the results of W. Heuse and J. Otto of Germany, W. H. Keesom et al. of the Netherlands, J. A. Beattie et al. of the U.S.A. and M. Kinoshita and J. Oishi of Japan are noted for their high precision. Their values are found to lie between 273.149 and 273.174.

Considering these results and the fact that the triple point of pure water is very near to 0.0100^oC, the 10th General Conference on Weights and Measures in 1954 decided to use the triple point of the water as the fixed point and to assign the value 273.16 as its temperature. It also redefined the thermodynamic Celsius temperature t^oC as t = T-273.15, where T is the value of the absolute temperature determined from the above decision. The zero of the new thermodynamic Celsius temperature differs by about 0.0001^o from the ice point.

For ordinary purposes, the differences in these new and old scales are quite negligible. However, for cases where a precision of $1O^{-4}$ degree in the absolute value is required, we must take the differences into consideration.

2.5. *Divertissement* 8: On the names of thermodynamic functions

The word "energy $\epsilon\nu\epsilon\rho\gamma\epsilon\iota\alpha$" can be seen in the works of Aristotle but "internal energy" is due to W. Thomson (1852) and R. J. E. Clausius (1876). The portion "en" means *inhalt*=capacity and "orgy", like the unit "erg", derives from $\epsilon\rho\gamma o\nu$=work. "Entropy" is also attributed to Clausius (1865) who took it from $\epsilon\nu\tau\rho\epsilon\pi\epsilon\iota\nu$=verwandeln and means *verwandlungsinhalt*=change quantity. "Enthalpy" was introduced by H. Kamerlingh Onnes (1909) from $\epsilon\nu\theta\alpha\lambda\pi\epsilon\iota\nu$=sich erwarmen which means *warmeinhalt*. J.W. Gibbs called it the heat function (for constant pressure). "Free energy" is due to H. van Helmholtz (1882), and means that part of the internal energy that can be converted into work, as seen in the equation dF=d’A for an isothermal quasi-static process. It was customary to call the remaining part, TS, of the internal energy, U = F + TS, the *gebundene energie* (bound energy), but this is not so common now. The Gibbs free energy (for constant pressure) was introduced by Gibbs, but German scientists used to call it *die freie enthalpie*. Thus the thermodynamic functions often have different names in

German and in English.

Further, on the equation of state: Kamerlingh Onnes gave the names, *thermische zustandsgleichung* to $p = p(T, V)$ and the name *kalorische zustandsgleichung* to $E = E(S, V)$. M. Planck (1908) called the latter *kanonische zustandsgleichung*.

3. Some Properties of Ideal and Non-Ideal Materials

3.1. Ideal Gases

Very dilute gases obey the so-called ideal gas law or equation of state, initially deduced from Boyle's Law* and Charles's Law†, which when combined show that

$$PV = NRT, \tag{3.1}$$

where

SI Units for some common quantities arising in the study of gases.

Symbol	Name	SI Abbreviation	SI Unit
P	Pressure (Pascale)	Pa	$kg/(m\ sec^2)$
V	Volume	m^3	
N	Number of moles.	mol	moles
T	Absolute Temperature	K	Kelvin
R	Gas Constant	8.314442	$J/(K\ mol)$
N_A	Avogadro's Number	6.0225×10^{23}	$molecules/mol$

Note that 1 standard atmosphere is $1.01325 \times 10^5 Pa = 101.325 kPa$. Under Standard Temperature and Pressure (STP) conditions $T \equiv 273.15K$ $(0C)$ and $P \equiv 101.325kPa$ (1ˆatm); hence, by rearranging Eq. (3.1) we see that $\bar{V} \equiv V/N = RT/P = 0.0224\ m^3/mol$, or more commonly as $22.4\ liters/mol$.

3.2. Dalton's Law

In mixtures of dilute gases, Dalton‡ showed that the ideal gas equation, cf., Eq. (3.1), needed to be modified by replacing N by the total number of moles in the gas, i.e., $N \to N_{total} \equiv \sum_i N_i$, i.e.,

$$P = \frac{RT}{V} \sum_i N_i = \sum_i P_i, \tag{3.2}$$

where

$$P_i \equiv N_i RT/V = x_i P, \tag{3.3}$$

is known as the partial pressure and is the pressure a pure gas of component i would have for a given molar volume and temperature. We have also introduced the mole fraction, $x_i \equiv N_i/N_{total}$, in writing the last equality. Since $\sum_i x_i = 1$, it can be summed to give Eq. (3.2).

---

*Robert Boyle, 1627-1691, showed that $P \propto 1/V$.

†Jacques Alexandre César Charles, 1746-1823, showed that $V \propto T$.

‡John Dalton, FRS, 1766-1844.

You might think that the partial pressure concept is some sort of mathematical game and that the partial pressures are not physically relevant. After all, only N_{total} matters in the equation of state. As Dalton showed, this is not correct. To see why, consider the following experiment.

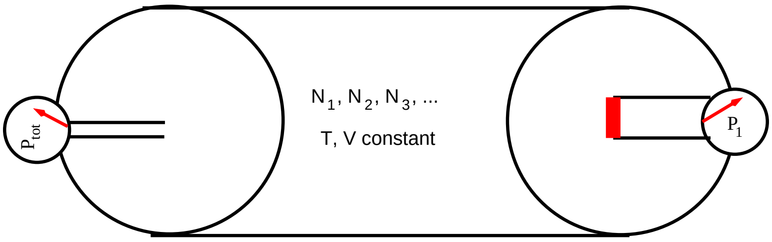


Fig. 3.1. Dalton's Experiment: a rigid cylinder containing a gas mixture at temperature T and N_i moles of gas "i". Two pressure measuring devices (e.g., manometers) are attached to the cylinder. The one on the left is directly connected to the gas mixture via a hole (or valve) in the top of the cylinder. The meter on the right is connected to the mixture through a porous plug that only allows component 1 to pass.*

As expected, the left meter reads P_{total} in accord with Dalton's Law. The meter on the right reads P_1, the partial pressure of the permeable component. Thus, in establishing its equilibrium with the meter, the permeable component acts as if the other components weren't there! As we shall see later, this plays a central role in chemical equilibrium..

3.3. Beyond Ideal Gases

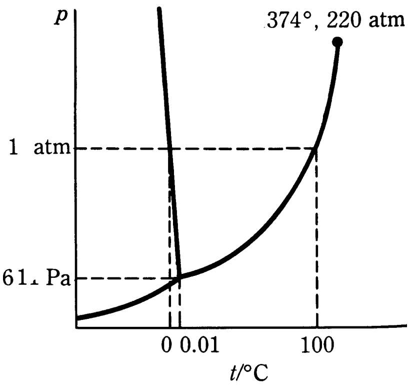


Fig. 3.2. Phase diagram of water.[1] Shown are the coexistence lines for gas-solid (sublimation), gas-liquid (vaporization or condensation), and liquid-solid (freezing or melting) lines. The point where all three meet is known as the triple point. The liquid-vapor line terminates at the so-called critical point. Finally, for water, note that there are several solid-solid coexistence lines (not shown) at even lower temperatures and/or higher pressures.

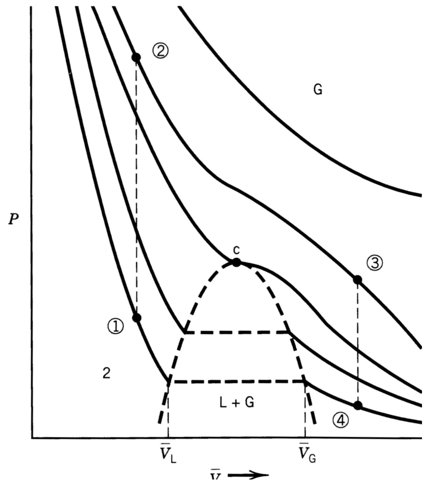


Fig. 3.3. Liquid-vapor pressure-volume phase diagram near the critical point.[2] The solid curves are known as isotherms (constant temperature) and the dashed lines correspond to liquid-vapor phase equilibrium where low (gas, $\bar{V}_G$) and high (liquid, $\bar{V}_L$) phases coexist. Two features of interest are the critical point, labeled c, and a path ($1 \rightarrow 2 \rightarrow 3 \rightarrow 4$) whereby a liquid is vaporized without boiling.

*For example, thin Pd sheets are porous to H_2 and not much else. Alternately, small-pore zeolites can also be used to filter/selectively pass gases.

Figures 3.2 and 3.3 show examples of pressure-temperature and pressure-volume phase diagrams, respectively. Many of the details contained in these phase diagrams will be considered next term. For now, simply note that Fig. 3.3 shows that ideal gas behavior is observed only at high enough temperature and molar volume. Also note that only the liquid-gas equilibrium's show critical points. That's because liquids and gases differ only in details (e.g., density, index of refraction, etc.) and not in symmetries, i.e., both are isotropic and homogeneous, something that solids are not by virtue of their crystal lattices.

There are many objections that can be raised against the ideal gas and Dalton's laws. Here are a few: a) why don't they depend on the chemical identity of the gas? b) they predict finite pressure for all but $\bar{V} \to 0$; and c) they predict vanishing volume as $T \to 0K$. Some of these objections can be dismissed if we consider how far apart the gas molecules are under typical conditions, i.e., around ambient temperature and pressure.

According Eq. (3.3), under STP conditions, the volume per molecule is $\bar{V}/N_A = 0.0224\ m^3/6.0225 \times 10^{23} = (33.39 \times 10^{-10} m)^3$. Thus, we see that the typical distance between molecules in this gas is $33.39\mathring{A}$, which is large compared to the size of gaseous elements and many small molecules. Nonetheless, the distance shrinks as the pressure increases or in condensed liquid or solid phases. For example, given that the molar volume of water (molecular weight 18 g/mol, density at STP 1 g/cm^3) is $18cm^3/mol$ or $2.98 \times 10^{-23} cm^3/molecule$ we see that the typical distance between water molecules is around $3.1\mathring{A}$, which is approximately the size of a water molecule; hence, in liquid water the molecules are more or less in direct contact, and we would expect that molecular details (geometry, bonding, dipole moment, etc.) to play an important role, as they do.

This discussion can be made more quantitative if we consider the so-called compressibility factor or ratio, Z,

$$Z = \frac{P\bar{V}}{RT} = \frac{\bar{V}}{\bar{V}_{ideal}}\,, \tag{3.4}$$

where $\bar{V}_{ideal} = RT/P$ is the molar volume an ideal gas would at the same temperature and pressure. Some examples for the van der Waals model are shown in Fig. 3.4.

One general way to deal with deviations from ideal behavior in the gas phase, at least for low densities, is to write down the so-called virial expansion* In more modern terms, the virial expansion is a Taylor polynomial approximation, i.e.,

$$Z = 1 + Bn + Cn^2 + \ldots = \sum_{i=1} B_i n^{i-1}, \tag{3.5}$$

where $n \equiv 1/\bar{V}$ is the molar density, and where B and C are known as the second and third viral coefficients, respectively. The second equality is an alternate notational convention with $B_1 = 1$,

[1] G. W. Castellan, *Physical Chemistry, 3rd ed.*, (Benjamin Pub. Co., 1983), p. 266.

[2] R.J. Silbey and R.A. Alberty, *Physical Chemistry, 3rd ed.*, (John Wiley & Sons, Inc. 2001) p. 16.

*Virial n. [L. vis, viris, force.] A certain function relating to a system of forces and their points of application, -- first used by Clausius in the investigation of problems in molecular physics/physical chemistry. [1913 Webster]

$B_2 = B$, $B_3 = C$, etc.. In general, the virial coefficients are intensive functions of temperature and has units of volume^{i-1}.

The theoretical tools required to calculate the virial coefficients were developed in the mid 20th century and we've been able to calculate the first 10 for model potentials of molecular interaction. Less well understood is the radius of convergence of the virial expansion, an important question, if we would like to somehow extrapolate to the liquid phase. According to the Lee-Yang theorem,† the radius of convergence is the condensation density, which means that the series cannot be used to study the liquid phase directly.

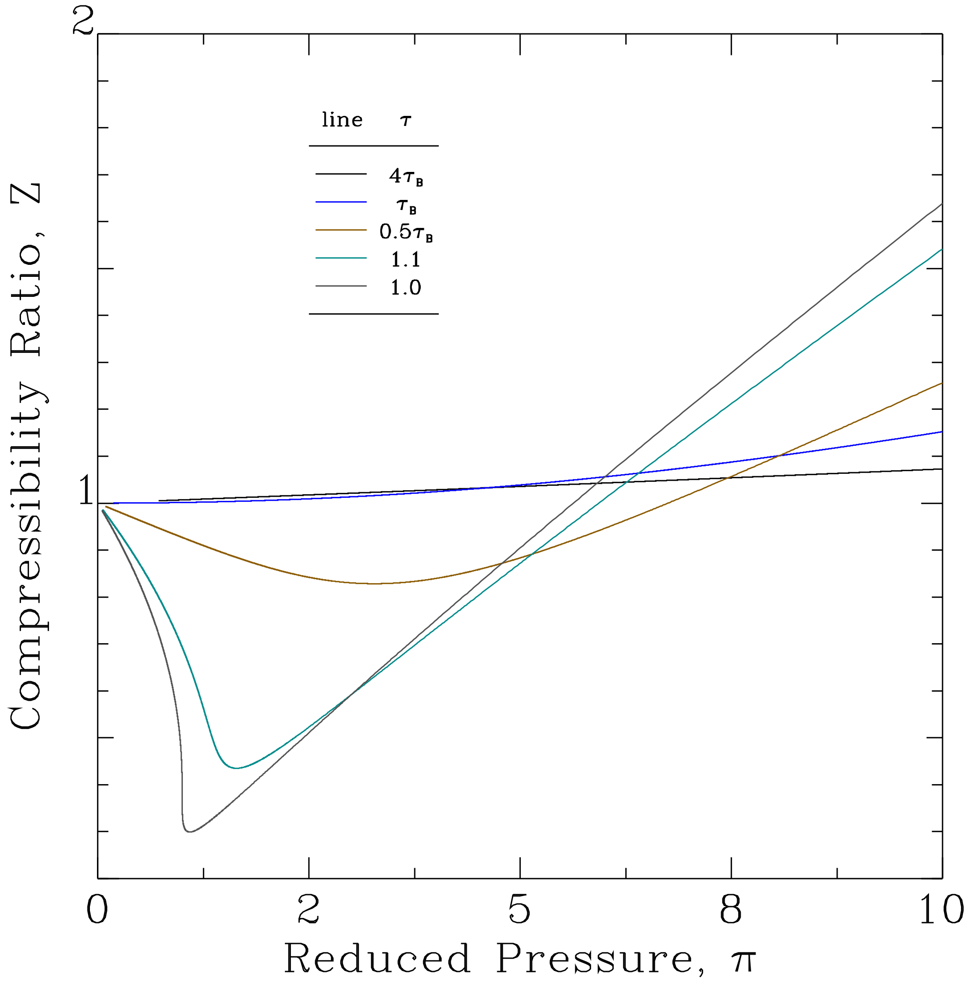


Fig. 3.4. The compressibility factor for the van der Waals model (see below for an explanation of reduced variables). Note that both positive and negative deviations from $Z = 1$ are possible. The change-over temperature, the so-called reduced Boyle temperature, τ_B, is that where attractive and repulsive interactions balance and the second virial coefficient vanishes. For the van der Waals model $T_B = a/Rb$ which leads to $\tau_B = 27/8 = 3.375$.

†C.N. Yang and T.D. Lee, *Statistical Theory of Equations of State and Phase Transitions. I. Theory of Condensation*, Phys. Rev. **87**, 404-409, (1952); T.D. Lee and C.N. Yang *Statistical Theory of Equations of State and Phase Transitions. II. Lattice Gas and Ising Model* Phys. Rev. **87**, 410-419, (1952). Note that these papers are well beyond your current mathematics and physics skills.

One of the first attempts at writing an equation of state that had liquid and vapor phases was due to the Dutch physical chemist van der Waals‡ The van der Waals model considers the repulsive and attractive interactions separately. First, it corrects for the intrinsic or steric volume per molecule by replacing the system's volume V by $V - Nb$, where b, known as the van der Waals b coefficient, and can be thought of as the minimum volume occupied by a mole of molecules, assuming that they don't deform at high pressure. Note that this won't be the geometric volume of the molecule, since some space is wasted due to packing considerations.

The second idea was to suggest that there are weak attractive forces between molecules (due to the so-called London dispersion forces). The attractions lead to the formation of weakly bound van der Waals dimers, thereby reduce the total number of molecules in the system. Since $PV = NRT$ anything that reduces N lowers the pressure.

To quantify this last idea, consider the dimerization reaction

$$2A \overset{K}{\rightleftarrows} A_2, \tag{3.6}$$

where K is the equilibrium constant for the reaction, and is very small for van der Waals dimers. At equilibrium,

$$\frac{[A_2]}{[A]^2} = K, \tag{3.7}$$

where $[A]$, etc., denote molar concentrations. Since A is conserved in the reaction,

$$[A]_{total} \equiv [A] + 2[A_2] \tag{3.8}$$

is constant, and can be used to eliminate $[A_2]$ from Eq. (3.7), which becomes

$$2K[A]^2 - [A]_{total} + [A] = 0. \tag{3.9}$$

This quadratic equation has one physical (positive) root, namely,

$$[A] = \frac{-1 + (1 + 8K[A]_{total})^{1/2}}{4K}\,. \tag{3.10}$$

By using this in Eq. (3.8) we can easily find $[A_2]$, and finally,

$$\bar{N} \equiv [A] + [A_2] = \frac{[A]_{total} + [A]}{2} = \frac{4K[A]_{total} - 1 + (1 + 8K[A]_{total})^{1/2}}{8K} \tag{3.11a}$$

$$\sim [A]_{total} - K[A]_{total}^2 + \ldots\,, \text{ for } K[A]_{total} \ll 1. \tag{3.11b}$$

‡Johannes Diderik van der Waals, 1837-1923, was the first to suggested how repulsive and attractive forces (now known as van der Waals or London dispersion interactions) lead to the existence of different phases and a critical point.

Where the last result was obtained by noting that $(1+x)^{1/2} \sim 1 + x/2 - x^2/8 + \ldots$ for $|x| \ll 1$. In short, the dimerization reaction leads to a reduction in the molar density proportional to $\bar{V}^{-2}$.

By combining the results of our discussion of the roles of repulsions and attractions, we can write down the van der Waals equation of state

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}, \tag{3.12}$$

where a, the van der Waals "a" constant, is the proportionality constant characterizing the reduction of N due to attractions. Some results are shown in Fig. 3.5.

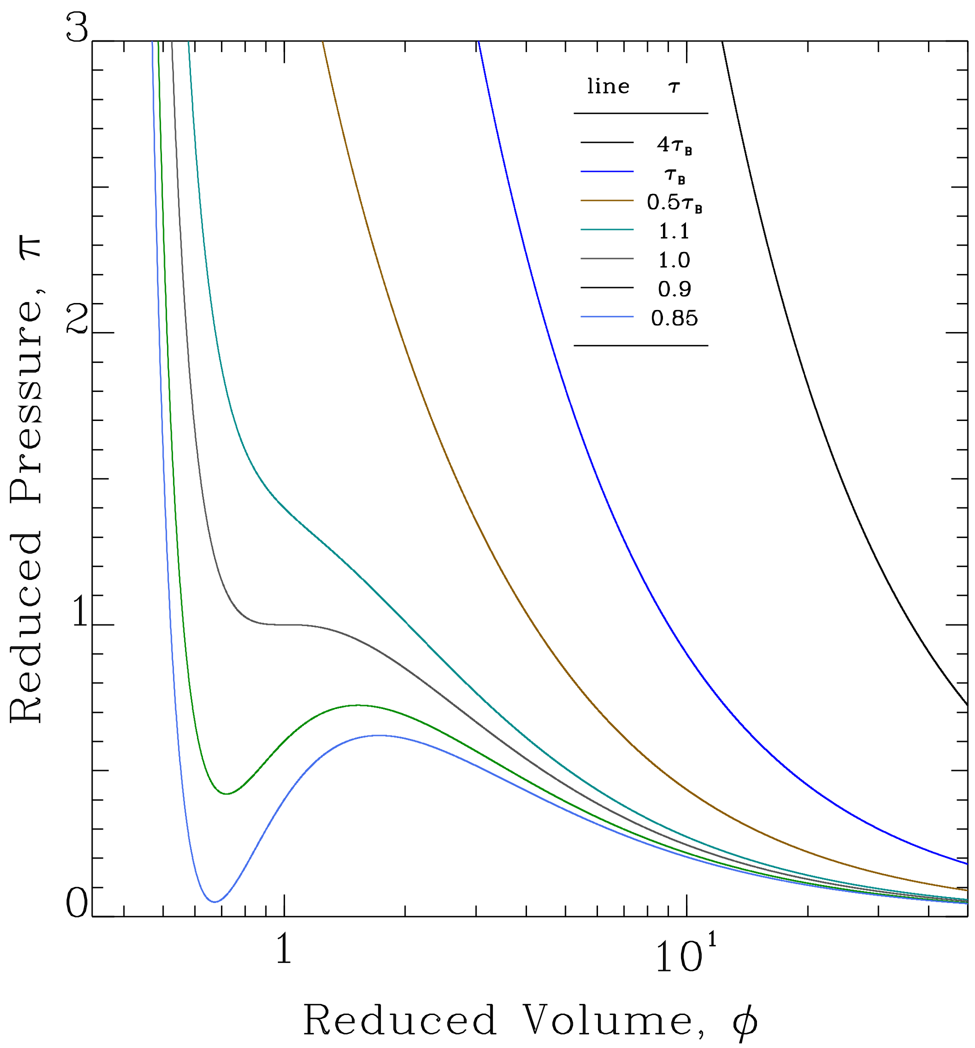


Fig. 3.5. Semi-log plots of the reduced pressure versus reduced volume for isotherms obtained using the van der Waals equation of state. The reduced pressures diverge as $\phi \to 1/3$ and become ideal as $\phi \to \infty$, cf. Eq. (3.12).

Notice the inflection point at the critical point. For temperatures below the critical temperature three states are possible, one at small ϕ one at large ϕ, and one in the middle. It is reasonable to identify the two outermost as a liquid and gas, respectively. The state in the middle is unphysical because its slope is positive; i.e., its molar volume increases with increasing pressure and leads to a negative compressibility.

Other thermodynamic quantities are easily found for the van der Waals model. For example the compressibility factor becomes:

$$Z = \frac{1}{1 - b/\bar{V}} - \frac{a/RT}{\bar{V}}\,. \tag{3.13}$$

and finally, the thermal expansion coefficient is found by differentiating the van der Waals equation, with respect to T keeping $Pconstant$. Some examples are shown in Fig. 3.4. Note that the compressibility diverges at the critical point, cf. Eq. (3.15) below.

We can make contact with the virial expansion, cf. Eq. (3.5), by recalling the geometric series

$$\frac{1}{1-x} \sim 1 + x + x^2 + x^3 + \ldots,$$

which when used in Eq. (3.13) shows that

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \left(\frac{b}{\bar{V}}\right)^3 + \ldots\,. \tag{3.14}$$

Thus, $B_2 = b - a/RT$ and $B_i = b^{i-1}$, for $i \geq 3$. The higher order virial coefficients are simply related to the excluded volume effects characterized by powers of the van der Waals b coefficient. This is probably not correct.

Only the second virial coefficient, $b - a/RT$, is nontrivial. First note that it can be positive (e.g. as in H_2) or negative (e.g., as in N_2) depending on whether repulsions or attractions are more important, particular, in particular, it will be positive for large temperatures and negative for low temperature.* The model predicts a zero initial slope when $T = T_B \equiv a/(Rb)$, known as the Boyle temperature. Physically, it is the temperature at which attractions and repulsions balance each other and the gas behaves more ideally than expected.

Perhaps the most interesting feature of the van der Waals model is the existence of the so-called critical point; i.e., the one where the differences between the liquid and vapor phases vanish (see, e.e., point c in Fig. 3.3). This implies that one can choose a path (such as $1 \to 2 \to 3 \to 4$) which starts with a high-density (liquid) phase and ends up as a low density (gas) phase without ever have 2 phase coexistence (no bubbles form and the system doesn't boil). This was controversial in the 19th century, but is now well established.

The critical state is the inflection point on the critical isotherm, cf. Figs. 3.3 or 3.5; i.e., where the first and second derivatives of the pressure-volume critical curve vanish. For the van der Waals model this implies that

$$0 = \left(\frac{\partial P}{\partial \bar{V}}\right)_T = -\frac{RT}{(\bar{V}-b)^2} + \frac{2a}{\bar{V}^3} \text{ and } 0 = \left(\frac{\partial^2 P}{\partial \bar{V}^2}\right)_T = \frac{2RT}{(\bar{V}-b)^3} - \frac{6a}{\bar{V}^4}\,, \tag{3.15}$$

*This assumes that a and b don't depend on temperature.

cf. Eq. (3.12). These can be solved for a and b, giving

$$b = \frac{\bar{V}_C}{3} \quad \text{and} \quad a = 3P_c\bar{V}_C^2, \tag{3.16}$$

or

$$\bar{V}_C = 3b,\ \ T_C = \frac{8a}{27Rb}\ , \ \text{and}\ \ P_c = \frac{a}{27b^2}\ , \tag{3.17}$$

where we have used Eq. (3.12) to get the critical pressure P_C .

Something interesting happens if we introduce reduced variables, i.e.,

$$\pi \equiv \frac{P}{P_C}\ ,\ \ \tau \equiv \frac{T}{T_C}\ ,\ \text{and}\ \ \phi \equiv \frac{\bar{V}}{\bar{V}_C}\ , \tag{3.18}$$

all of which are dimensionless. By using the reduced variables and Eq. (3.17) we can rewrite the van der Waals equation, Eq. (3.12), as

$$\pi = \frac{8\tau}{3\phi - 1} - \frac{3}{\phi^3}\ . \tag{3.19}$$

All material dependent parameters (e.g., a and b) have canceled out. Hence, *if the van der Waals model were exact*, equations of state plotted in terms of reduced variables would give the same curves, cf. Figs. 3.4 and 3.5. The materials are said to be in corresponding states. This phenomena is known as the law of corresponding states or universality. Note that this can be done for any 2 parameter model. In reality, the "law" is only an approximation.

In summary, the van der Waals equation is qualitatively correct, predicting 2-phase coexistence, a critical point, and universal* behavior. On the other hand, it is quantitatively incorrect, and in practice, other models are used. Problem 3 of problem set 1 explores this claim more carefully.

3.4. Liquids and Solids

Depending on the question asked, solids and liquids can be easier or harder to treat than gases. For example, since both are difficult to compress, linear approximations are often satisfactory, e.g.,

$$\frac{\Delta V}{V} \approx -\kappa \Delta P, \tag{3.20}$$

where the isothermal compressibility, κ, is defined as

*The story is a bit more complicated. It turns out that many disparate materials exhibit universality close enough to the critical point. An interesting observation because all of the classical models, while exhibiting universal behavior, fail to describe many of the basic details of the behavior close to the critical point. This was sorted out in the 1970's by B. Widom (chemistry), M. E. Fisher (chemistry), L. Kadanoff (physics), and K.G. Wilson (physics), and led to Wilson winning the 1982 Nobel prize in physics.

$$\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{N,T}. \tag{3.21}$$

Notice the explicit - sign in the definition of κ. All stable materials have positive κ (things get smaller when you squeeze them). The factor of 1/V makes κ intensive, and therefore easier to tabulate.

The isothermal compressibility, becomes $1/P$ for the ideal gas, or more generally for the van der Waals liquid or gas

$$\kappa = -\left[\bar{V}\left(\frac{\partial P}{\partial \bar{V}}\right)_{T,N}\right]^{-1} = \left(\frac{RT\bar{V}}{(\bar{V}-b)^2} - \frac{2a}{\bar{V}^2}\right)^{-1}, \tag{3.22}$$

cf. Eq. (3.15).

Similarly, for small temperature changes,

$$\frac{\Delta V}{V} \approx \alpha \Delta T, \tag{3.23}$$

where the (isobaric or constant pressure) thermal expansion coefficient, α, is defined as

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{N,P}. \tag{3.24}$$

Like κ, the factor of 1/V makes α intensive. However, unlike κ, the thermal expansion coefficient can be positive or negative (e.g., it vanishes for liquid water at 4C and 1 atm). For the ideal gas, $\alpha = 1/T$, while for the van der Walls gas or liquid

$$\alpha = \left[\frac{(\bar{V}-b)}{R}\left(\frac{RT\bar{V}}{(\bar{V}-b)^2} - \frac{2a}{\bar{V}^2}\right)\right]^{-1}, \tag{3.25}$$

which is obtained by differentiating the van der Walls equation of state with respect to temperature keeping pressure constant, using the chain rule, noting that $(\partial\bar{V}/\partial T)_P = \bar{V}\alpha$, and the solving the resulting equation for α.

For so-called ideal solids, these being crystalline materials with roughly harmonic interatomic interactions, one can go considerably farther in calculating mechanical quantities like κ and α, as well as elastic constants, heat capacities, energies, electronic properties, etc.; this is well beyond the scope of this course.* Liquids are less tractable than solids having the same complications arising from the molecules being close together without the simplifications associated with having an underlying periodicity or crystal lattice. At present, complex liquids are studied theoretically by using brute force methods like Monte Carlo or molecular dynamics computer simulations.

---

*However, see, e.g., M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, (Clarendon Press, 1962).

4. Probability and Statistics

As we have stressed in class, when dealing with a macroscopic sample of a material it is practically impossible to measure or calculate all the microscopic properties of the ~ 10^{23} atoms or molecules in the system. Fortunately, many kinds of phenomena do not depend on the precise behavior of any single particle, and only average properties of the constituent particles are important. In order to quantify these averages, we must consider some simple ideas in probability and statistics.

We all encounter probabilistic concepts in daily life. Results of opinion polls, life expectancy tables, and grade distributions are but a few examples. Shown below, are two grade distributions for two classes taking an hourly exam in some course.

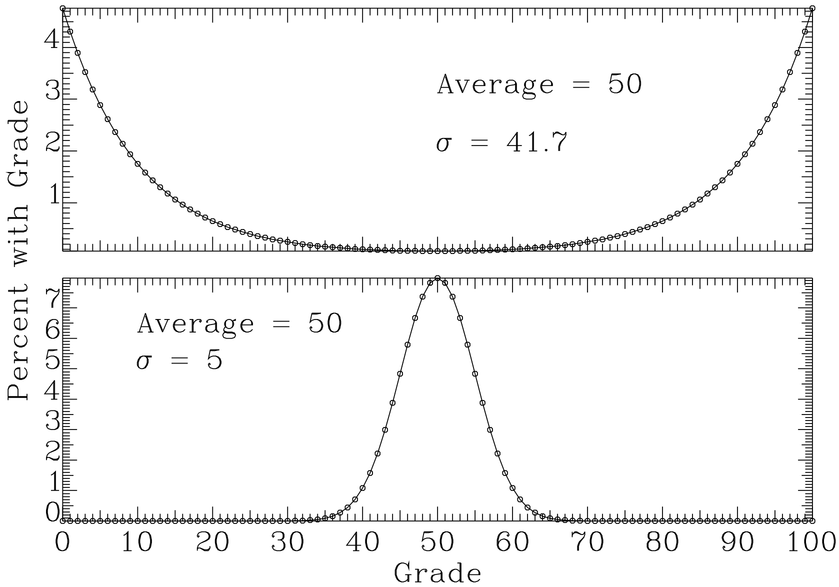


Fig. 4.1. Two hypothetical grade distributions with the same mean

How would you use this information?

Perhaps the simplest quantity to compute is the average grade; i.e.,

$$AVERAGE\ GRADE = \sum_{i=0}^{100} \frac{N(i)}{N_{total}}\ i, \tag{4.1}$$

where $N(i)$ is the number of students with grade i and N_{total} is the total number of students in each class. Notice that even though the two distributions are very different, they have the same average grade.

How much information is contained in the average grade and how relevant is the average to any individual in the class? In the hypothetical distribution the average tells the whole story. The distribution is extremely narrow, and thus practically everyone got the average grade. The same is not true in the real distribution; there is a significant spread in the scores. This spread can be quantified by defining the probability, P(i), of finding any student with grade i. For this example,

$$P(i) \equiv \frac{N(i)}{N_{total}} \tag{4.2}$$

which is simply the faction of students with grade i. Notice that probabilities are "normalized" in the sense that

$$\sum_i P(i) = 1. \tag{4.3}$$

This is just a complicated way of stating the fact that every student taking the exam receives some grade.

A measure of the width of the distribution can be obtained by computing the standard deviation. If we denote the average grade by <i>, then the standard deviation, σ, is defined as:

$$\sigma^2 \equiv \sum_i P(i)\ [\ i - < i >\ ]^2 \tag{4.4}$$

(Note, σ is the Greek letter sigma).

When we consider atomic and molecular systems the situation becomes somewhat more complicated, although the basic ideas are the same as those introduced in the grade example discussed above. You have already used probability when you learned about atomic and molecular orbitals. In the kinetic theory of gasses, a different sort of question is being asked; namely, how do the molecules move?

To be specific, suppose we want the distribution of velocities in the x direction for a sample of gas containing 10^{23} molecules. Even if we ignore the experimental impossibility of measuring the velocities of all of the molecules, what would we do with this huge amount of information? It would be useful to make the kind of histogram used in discussing grade distributions; however there is an additional complication. For the exam discussed above, no fractional grades were assigned, and thus there is a natural bin width of 1 grade point. On the other hand, nature does not assign discrete values to the x components of the molecular velocities. Hence, if we were to make our bins too small in constructing our histogram, most of them would contain only 0 or 1 particles, even for a sample containing 10^{23} particles.

In order to get around this difficulty, we must include some information about the size of the "bin" in our introduction of probability. This is done by defining **probability density**, $f(v_x)$:

$$f(v_x)\ \Delta v_x \equiv \begin{cases} \text{The probability that a molecule has} \\ \text{velocity between } \mathrm{v_x} \text{ and } \mathrm{v_x} + \Delta \mathrm{v_x} \end{cases}$$

Notice that the bin size is explicitly contained in our definition and is responsible for the probability of an infinitely precise result, i.e., $\Delta v_x = 0$, vanishes. Also note that in general probability densities have units (in this example the units are inverse velocity).

Once we know the probability density, averages can be computed just as in the grade example considered above. For example,

$$< v_x^n > = \sum_{v_x} v_x^n \ f(v_x) \ \Delta v_x. \tag{4.5}$$

Throughout this part of the course, we will denote average quantities by surrounding them with "< >". What should this average be for n=0 or 1? What is the physical significance of the average for n=2?

Of course, typical samples of the gas contain a large number of particles, and thus, the bins can be taken to be very small. What does the sum in Eq. (4.5) become in this limit? We know that this is an integral, and we therefore rewrite Eq. (4.5) as

$$< v_x^n > = \int_{-\infty}^{\infty} v_x^n \ f(v_x) \ dv_x. \tag{4.6}$$

Finally, one more aspect of probability must be considered. In the molecular velocity example, we discussed only the x component. However, velocity is a vector and there are also the y and z components. How would we describe the probability that any molecule is traveling in some specific direction? Clearly, for molecules in a gas, the probability that the x component of the velocity lies in some interval should be independent of what the other two components are doing. For such situations, the probability that a molecule has velocity with components in the intervals v_x to $v_x + \Delta v_x$, v_y to $v_y + \Delta v_y$, and v_z to $v_z + \Delta v_z$ is

$$F(v_x, v_y, v_z)\Delta v_x \Delta v_y \Delta v_z = f(v_x) f(v_y) f(v_z) \Delta v_x \Delta v_y \Delta v_z. \tag{4.7}$$

If you are having trouble believing this, consider the probability that three coins come up heads or tails in any set of three of tosses. This is a model the velocity probability distribution in a universe were all the magnitudes of the velocity components in the three directions are equal.

Further aspects of probability densities in gas kinetics will be discussed in class, but this material should get you started.

5. Maxwell-Boltzmann Distribution

The molecular description of the bulk properties of a gas depends upon our knowing the mathematical form of the velocity distribution; That is, the probability, $F(v_x, v_y, v_z)\Delta v_x \Delta v_y \Delta v_z$, of finding a molecule with velocity components in the range v_x to $v_x + \Delta v_x$, v_y to $v_y + \Delta v_y$, and v_z to $v_z + \Delta v_z$ (see the last chapter). This can be found by making two very simple assumptions:

a) All directions are equivalent (space is isotropic). This implies that the probability of finding a molecule moving with a certain velocity cannot depend on the direction; it is equally probable to find a molecule with any speed v moving in any direction. Mathematically, this implies that the probability density can only depend on the magnitude of the velocity, or the molecular speed. Hence,

$$F(v_x, v_y, v_x) = F([v_x^2 + v_y^2 + v_z^2]^{1/2}). \tag{5.1}$$

b) The three components of the velocity are independent of each other. This implies that the velocity probability density can be written as:

$$F(v_x, v_y, v_x) = f(v_x)f(v_y)f(v_z) \tag{5.2}$$

By comparing Eqs. (5.1) and (5.2), we have

$$f(v_x)f(v_y)f(v_z) = F([v_x^2 + v_y^2 + v_z^2]^{1/2}). \tag{5.3}$$

Very few functions can satisfy Eq. (5.3); in fact, the only one is:

$$f(v_i) = Ae^{-bv_i^2}, \quad i = x, y, z, \tag{5.4}$$

where A and b are, as yet, arbitrary constants. Verify that f given by Eq. (5.4) satisfies Eq. (5.3). To show that Eq. (5.4) is the only possible function requires some mathematics which might be beyond the level of the course; nonetheless, the proof is contained in the appendix for those of you who are interested.

How do we determine the values of the constants A and b? The function f, is a probability density and every molecule must have some velocity. From the previous section, we know that this means

$$1 = \sum_{v_x=-\infty}^{\infty} f(v_x)\Delta v_x \to \int_{-\infty}^{\infty} f(v_x)dv_x, \tag{5.5}$$

where the integral is obtained when we make Δv_x very small. By going to a table of integrals we find that

$$\int_{-\infty}^{\infty} dv\ Ae^{-bv^2} = A\left(\frac{\pi}{b}\right)^{1/2}, \tag{5.6}$$

which when used in Eq. (5.5) gives

$$A = \left(\frac{b}{\pi}\right)^{1/2}. \tag{5.7}$$

The parameter b is found as follows: We will compute the pressure that a dilute gas exerts on the walls of its container and then compare the result with experiment (i.e., the ideal gas equation of state). What is the pressure and how do we get it from the velocity distribution? The pressure is the force exerted by the gas per unit area. Moreover, the force is the rate of change of momentum per unit time due to collisions with the wall.

Imagine the molecules which comprise our gas as billiard balls and assume that the walls are perfectly smooth. What happens when a molecule collides with the wall? Actually relatively little; the normal component of the velocity changes sign (see Fig. 5.1).

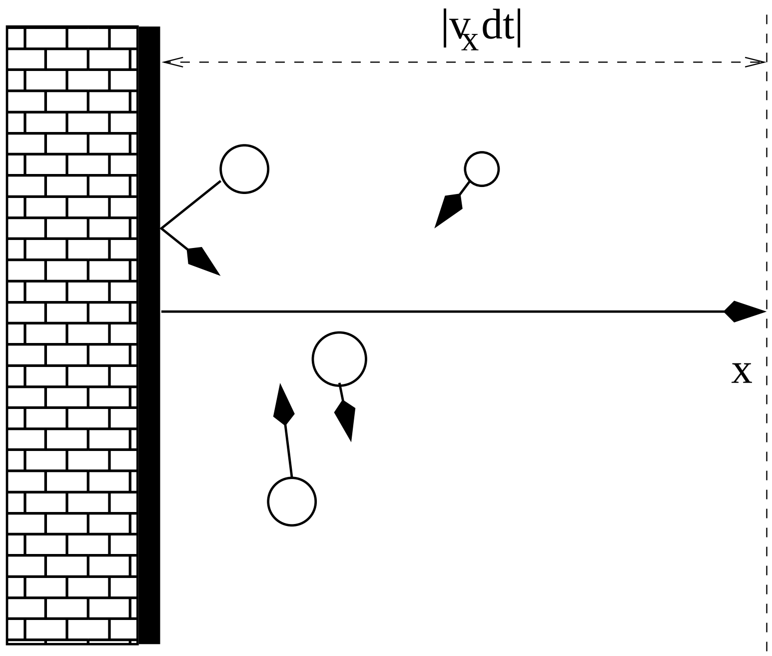


Fig. 5.1. Elastic collisions with a smooth wall of unit area.

If the wall is taken to be the y-z plane, the momentum change, ΔP, is

$$\Delta p = -2mv_x = -F_{x,\text{molecule on wall}}\Delta t, \tag{5.8}$$

where m is the mass of the molecule and where $F_{x,\text{molecule on wall}}$ is the x-component of the force exerted by the molecule on the wall when it collides. A typical velocity is 10^5 cm/sec; what is a typical momentum change for argon? How many molecules with velocity v_x will collide with the wall per unit area in time Δt? From Fig. 5.1, it should be clear that any molecule within a distance $v_x \Delta t$ will hit the wall in time Δt, assuming of course, that $v_x < 0$ for the way the figure was drawn (i.e., with the wall on the left). The number per unit area is therefore:

$$n(v_x)|v_x|\Delta t, \tag{5.9}$$

where $n(v)$ is the number of molecules per unit volume with x component of velocity in the range v_x to $v_x + \Delta v_x$. This is related to the molecular velocity distribution by

$$n(v_x) = n_0 f(v_x)\Delta v_x, \tag{5.10}$$

where n_0 is the number of molecules per unit volume. By multiplying Eqs. (5.8) and (5.9), then substituting according to Eq. (5.10), and dividing by Δt, we finally arrive at the pressure exerted by those molecules with x velocity component in the range v_x to $v_x + \Delta v_x$, $P_{v_x,\, v_x+\Delta v_x}$:

$$2mn_0 v_x^2 f(v_x)\Delta v_x = \frac{F_{v_x,v_x+\Delta v_x}}{Area} = P_{v_x,v_x+\Delta v_x}, \tag{5.11}$$

where $F_{v_x,v_x+\Delta v_x}$ is the contribution to the force on the wall from molecules with x velocity component in the range v_x to $v_x + \Delta v_x$. All that remains is to include the contributions from all velocities corresponding to molecules moving towards the wall. The total pressure, P, thus equals:

$$P = \sum_{v_x=-\infty}^{0} dv_x\ 2mn_0 v_x^2 f(v_x) = \int_{-\infty}^{0} dv_x\ 2mn_0 v_x^2 f(v_x) = \int_0^{\infty} dv_x\ 2mn_0 v_x^2 \left(\frac{b}{\pi}\right)^{1/2} e^{-bv_x^2}, \tag{5.12}$$

where the last equality comes from using the explicit form of the probability density, [see Eqs. (5.4) and (5.7)]. The value of the integral is:

$$\int_0^{\infty} dv_x\ v_x^2 e^{-bv_x^2} = \frac{1}{4b}\left(\frac{\pi}{b}\right)^{1/2}.$$

If we use this result in Eq. (5.12), we find that

$$P = \frac{mn_0}{2b}. \tag{5.13}$$

Next we write the ideal gas equation of state in terms of the number density:

$$P = n_0 k_B T,$$

where k_B is Boltzmann's constant:

$$k_B \equiv \frac{R}{N_A} = \frac{R}{6.0225 \times 10^{23}} = 1.38 \times 10^{-23} J/K.$$

By comparing this with Eq. (5.13) we see that

$$b = \frac{m}{2k_B T}.$$

The velocity probability density for the x component can now be written as

$$f(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{mv_x^2}{2k_B T}}, \tag{5.14}$$

or for the full velocity as

$$F(v_x, v_y, v_x) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{E}{k_B T}}, \tag{5.15}$$

where $E = m(v_x^2 + v_y^2 + v_z^2)/2$ is the kinetic energy of a molecule. This is referred to as the Maxwell-Boltzmann distribution function and is illustrated in the following figure:

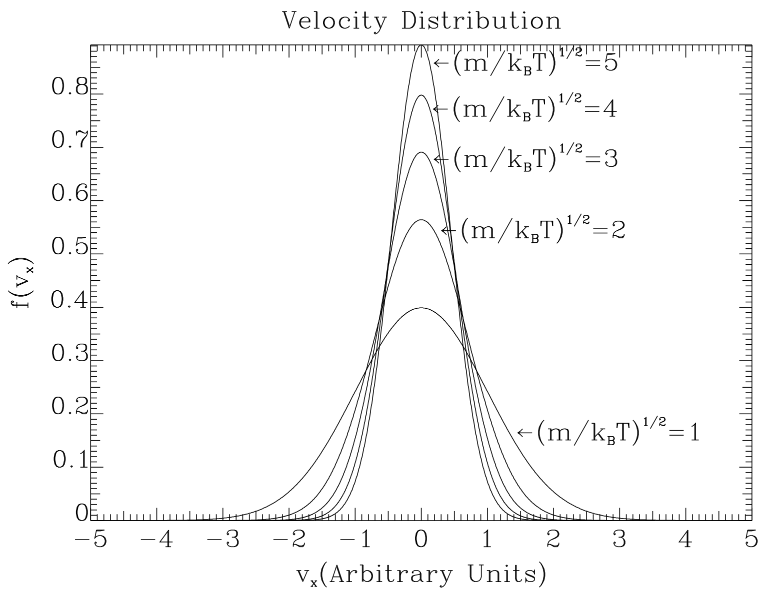


Fig. 5.2. The Maxwell-Boltzmann 1-D velocity distribution. Note that the probability of finding faster molecules is increased if we raise the temperature or lower the mass.

Notice that increasing the temperature or reducing the mass makes it more probable to find molecules with higher velocities and that the probability of observing any given velocity will decrease as the energy associated with that velocity increases. This last comment is not limited to our simple billiard ball model of the molecules.

What is the average kinetic energy of the molecules; i.e., what is

$$\langle \frac{m}{2}(v_x^2 + v_y^2 + v_z^2)\rangle = \frac{3m}{2}\langle v_x^2\rangle = \frac{3m}{2}\left(\frac{m}{2\pi k_B T}\right)^{1/2}] \int_{-\infty}^{\infty} dv_x\, e^{-mv_x^2/2k_B T} v_x^2 = \frac{3}{2} k_B T,$$

where the first equality follows from our assumption that all directions are equivalent and where the last uses the integral given above. Notice that the average kinetic energy is independent of the mass of the molecules and predicts a constant heat capacity; specifically

$$\bar{C}_V \equiv \left(\frac{\partial \bar{E}}{\partial T}\right)_{N,V} = \frac{3}{2} R.$$

This is well born out for noble gases and is an example of the so-called law of Dulong and Petit. For example, our result predicts a constant volume heat capacity of 12.471 J K^{-1} mol^{-1} the value in the CRC Handbook gives 12.472 J K^{-1} mol^{-1*} It turns out that our result is more general, in that it also applies to all molecules as long as rotation, vibration and electronic effects can be ignored. In addition, in molecular dynamics computer simulations the temperature is often defined in terms of the average kinetic energy.

For many applications, the full Maxwell-Boltzmann velocity distribution gives too much detail. In particular, remember that it is a probability density for the vector velocity. Suppose we are interested in some property which depends only on the speed of the molecules and not their direction. What is the probability density which describes the distribution of molecular speeds?

The speed distribution function, $F(c)\,dc$, is the probability of observing a molecule with a speed in the interval c to $c + dc$ irrespective of its direction. It can be obtained from the full velocity distribution, cf. Eq. (5.15), by integrating (summing) over the possible velocity directions, i.e.,

$$F(c)dc = \sum_{c\le|\vec{v}|\le c+dc} F(v_x, v_y, v_z)\Delta v_x \Delta v_y \Delta v_z = F(v_x, v_y, v_z)\Big|_{|\mathbf{v}|\,=\,c} \sum_{c\le|\vec{v}|\le c+dc} \Delta v_x \Delta v_y \Delta v_z. \tag{5.16}$$

The sums in these last equations are over all velocities such that the speed is between c and $c + dc$. The second equality comes from noting that F only depends on the magnitude of the velocity (see Eq. (5.15)). What is this last sum? $\Delta v_x \Delta v_y \Delta v_z$ is a volume element in a coordinate system whose axes are the components of velocity. The sum represents the volume between two concentric spheres of radius c and c+dc, respectively. Thus

$$\sum_{c\le|\vec{v}|\le c+dc} \Delta v_x \Delta v_y \Delta v_z = \frac{4\pi}{3}\left[(c+dc)^3 - c^3\right] \approx 4\pi c^2 dc, \tag{5.17}$$

where the last expression was obtained by expanding the products and dropping nonlinear terms in dc (remember that we will consider infinitesimally small dc). If we use Eq. (5.17) in (5.16), we find that

$$F(c) = 4\pi c^2 F(v_x, v_y, v_z)\Big|_{|\mathbf{v}|=c} = 4\pi c^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mc^2}{2k_B T}}. \tag{5.18}$$

This is the speed distribution and is shown in Fig. 5.3 below. Notice that it vanishes when $c = 0$ even though the velocity distribution is a maximum at zero velocity. Why?

There are various ways to characterize the molecular speed in the gas. For example, consider the most probable speed, c^*, is found by setting the c derivative of Eq. (5.18) to zero; i.e.,

$$0 = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mc^2}{2k_B T}}\ \frac{m}{k_B T}\ c\left(\frac{2k_B T}{m} - c^2\right),$$

which gives physical roots at $c = 0$ (a minimum) and at $c^* = (2k_B T/m)^{1/2}$, which is the

*Note, that the CRC reports $\bar{C}_P$. As we shall see later, $\bar{C}_P = \bar{C}_V + R$ for an ideal gas.

maximum. This can be compared with $\langle c \rangle = (8k_BT/\pi m)^{1/2}$ and $c_{RMS} \equiv \sqrt{\langle c^2 \rangle} = (3k_BT/m)^{1/2}$, cf. Eq. (5.19). Note that $c^* < \langle c \rangle < c_{RMS}$. All three results have the form $(k_BT/m)^{1/2}$ times some dimensionless number; the first factor has the units of speed (length / time) and must be there unless there is another quantity that has the units of speed, which is not the case here. The dimensionless number depends on the details of the question being asked.

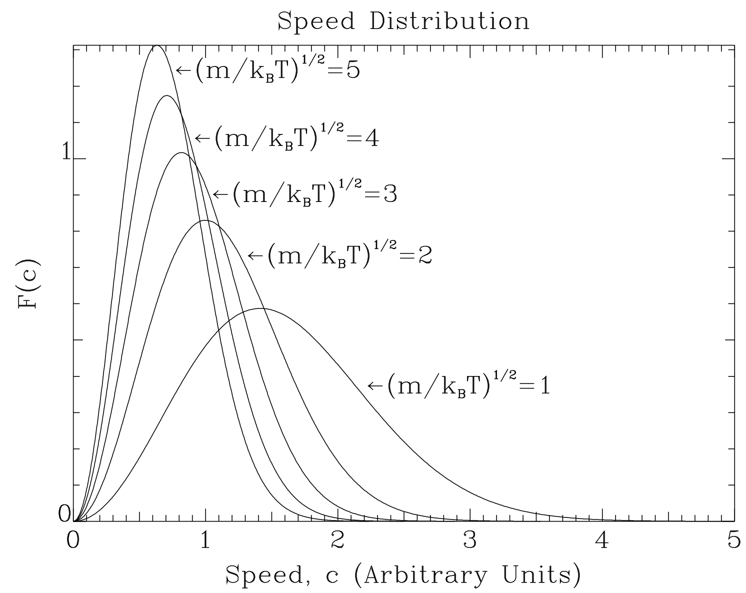


Fig. 5.3. The speed distribution for various temperatures and/or masses. As was the case with the velocity distribution, cf. Fig. 5.2, the probability of finding faster molecules increases if we raise the temperature of lower the mass.

The speed distribution is used to average quantities that don't depend on the direction the molecules are moving. Among these, the most useful are the mean-speed and root-mean squared speed (or velocity), $\sqrt{\langle c^2 \rangle}$, where

$$\langle c^n \rangle \equiv \left(\frac{m}{2\pi k_BT} \right)^{3/2} 4\pi \int_0^\infty dc\, c^{n+2} e^{-\frac{mc^2}{2k_BT}} = \begin{cases} \left(\dfrac{8k_BT}{\pi m} \right)^{1/2}, & n = 1 \\ \dfrac{3k_BT}{m}, & n = 2 \\ \left(\dfrac{2k_BT}{m} \right)^{n/2} \dfrac{2}{\sqrt{\pi}} \Gamma((n+3)/2), & \text{in general,} \end{cases} \tag{5.19}$$

where $\Gamma(x)$ is the gamma function and where a table of integrals can be used to look up these results. Notice that all the averages contain factors of $\sqrt{k_BT/m}$ which has units of velocity.

5.1. Appendix: Proof of Equation (5.4)

You are not responsible for this proof. Differentiate both sides of Eq. (5.3) with respect to v_x, using the chain rule for the right hand side, and divide by v_x. You get:

$$\frac{\dfrac{df(v_x)}{dv_x}\, f(v_y)\, f(v_z)}{v_x} = \frac{\left.\dfrac{dF(v)}{dv}\right|_{v=(v_x^2+v_y^2+v_z^2)^{1/2}}}{(v_x^2+v_y^2+v_z^2)^{1/2}}\,. \tag{5.20}$$

By repeating this for v_y, equating the results and carrying out a little algebra, we find that:

$$\frac{\dfrac{df(v_x)}{dv_x}}{v_x\, f(v_x)} = \frac{\dfrac{df(v_y)}{dv_y}}{v_y\, f(v_y)} \tag{5.21}$$

The right hand side of the equation depends only on v_y and the left hand side depends only on v_x. Since these two components of velocity can be chosen independently, the only way that this last equation can be satisfied is if both sides are equal to the same constant. Hence,

$$\frac{df(v_x)}{dv_x} = -2bv_x\, f(v_x), \tag{5.22}$$

where b is, as yet, some arbitrary constant. This is a first order differential equation. It has a general solution which will depend on a single multiplicative constant. This solution is given by Eq. (5.4).

6. Collisions, Reactions, and Transport

6.1. Effusion, Surface Collisions and Reactions

In the previous section, we found the parameter b by computing the average force exerted on the walls of the container. Suppose, instead, that the rate of collisions (i.e., the number of collisions per unit area per unit time) was desired. This is important for a number of practical considerations; e.g., if a chemical reaction takes place every time a molecule hits the surface, then the rate of the reaction will just be the collision rate.

We obtain the collision rate by repeating the analysis which determined the force on the wall in the previous section. Thus, the number of molecules per unit area with velocity v_x which collide in time interval Δt is

$$n(v_x)|v_x|\Delta t, \tag{6.1}$$

where we are using the same notation as in the preceding sections. The total number of collisions becomes:

$$Z_{wall}\Delta t = \int_{-\infty}^{0} dv_x\, n_0 \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_x^2/(2k_BT)}|v_x|\Delta t = \left(\frac{k_BT}{2\pi m}\right)^{1/2} n_0 \Delta t \tag{6.2}$$

Hence, the wall collision rate, Z_{wall}, is given by

$$Z_{wall} = \left(\frac{k_BT}{2\pi m}\right)^{1/2} n_0 = \tfrac{1}{4}\langle c\rangle n_0, \tag{6.3}$$

where $\langle c\rangle$ is the average speed, introduced in the preceding section. Aside from the previously mentioned example of chemical reaction on a surface, another application of this expression is in *effusion* though a pinhole. If there is a hole of area A in the surface, the rate that molecules escape the system is just $Z_{wall}A$. Notice that heavier molecules or isotopes will escape more slowly (with a $1/\sqrt{mass}$ dependence); hence, effusion through a pinhole is a simple way in which to separate different mass species.

The assumption that every collision leads to reaction is not quite right for many reasons (e.g., orientation of the molecule, its internal motion, etc.). The most important of these is easy to understand, namely, the molecule must have enough energy to overcome some sort of activation barrier. For our model this means that the molecule must be moving fast enough when it collides and this is easily incorporated into Eq. (6.2):

$$Z_{wall}^{reactive} = \int_{-\infty}^{-v_{\min}} dv_x\, n_0 \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_x^2/(2k_BT)}|v_x| = \tfrac{1}{4}\langle c\rangle n_0 e^{-E_a/k_BT}, \tag{6.4}$$

where $E_a \equiv \tfrac{1}{2} mv_{\min}^2$ is called the activation energy. This is just the well known Ahrennius behavior seen in most reaction rates. Note that plotting $\log(Z_{wall}^{reactive})$ vs $1/T$ would give an approximately straight line, and experimentally this is known as an Arrhenius plot.

6.2. Gas Phase Collisions and Chemical Reactions

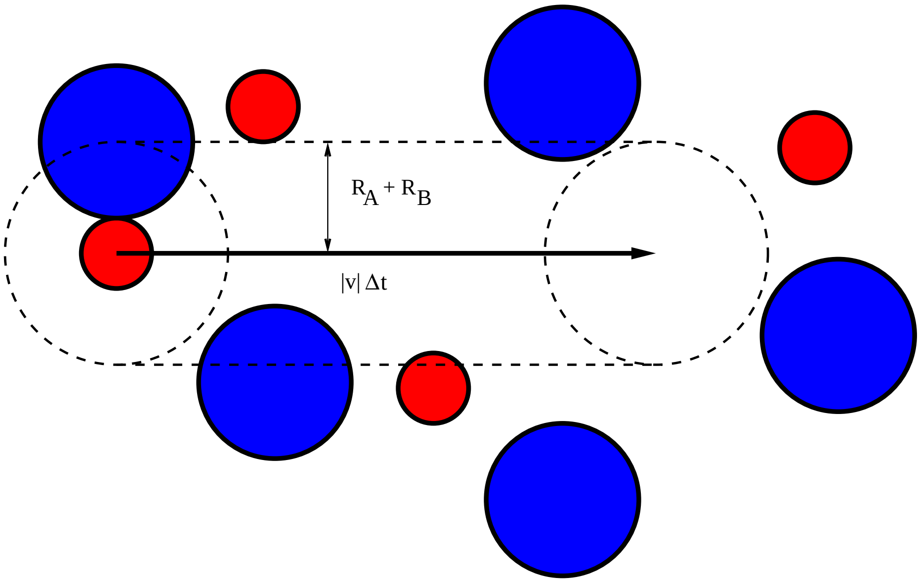


Fig. 6.1. Any blue molecule contained in the cylinder will collide with our red A molecule in time Δt

Next consider the number of collisions which a molecule of type A makes with those of type B in a gas. We will model the two molecules as hard spheres of radii R_A and R_B, respectively. Moreover, in order to simplify the calculation, we will assume that the B molecules are stationary (this is a good approximation if $m_B \gg m_A$). An A molecule moving with velocity $\vec{v}$ for time Δt will collide with any B molecule in a cylinder of radius $R_A + R_B$ (cf. Fig. 1) and length $|\vec{v}|\Delta t$. Hence, volume swept out will just be

$$|v|\Delta t \pi (R_A + R_B)^2, \tag{6.5}$$

and the actual number of collisions will $n_B \times$ volume swept out The average A-B collision rate, is obtained by multiplying by the probability density for A molecules with velocity $\vec{v}$ and averaging. Moreover, since only the speed of the molecule is important, we may use the molecular speed distribution function obtained in the preceding section to average over the speed of A. Thus, we get

$$Z_{A \text{ with } B's}\Delta t \equiv \int_0^\infty dc \left[4\pi c^2 \left(\frac{m_A}{2\pi k_B T} \right)^{3/2} e^{-m_A c^2/(2k_B T)} \right] \pi (R_A + R_B)^2 c \Delta t n_B, \tag{6.6}$$

where note that the quantity in the square brackets is just the seed probability density, $F(c)$. When the integral is evaluated, we find that

$$Z_{A \text{ with } B's} = \pi (R_A + R_B)^2 \langle c_A \rangle n_B, \tag{6.7}$$

where $\langle c_A \rangle$ is the average molecular speed of A; i.e.,

$$\langle c_A \rangle \equiv \left(\frac{8k_BT}{\pi m_A} \right)^{1/2}. \tag{6.8}$$

This is the number of collisions *one* A suffers in time Δt. The number of collisions with B's that all the A molecules in a unit volume suffer per unit time, $Z_{A,B}$, is

$$Z_{A,B} = n_A Z_{A \text{ with } B} = \pi(R_A + R_B)^2 \langle c_A \rangle n_A n_B. \tag{6.9}$$

As was mentioned at the outset, our expression is correct if the B's are not moving. It turns out that the correction for the motion of B is rather simple (and involves going to what is called the center-of-mass frame, which is not, but which is described in the Appendix); specifically, all we do is replace the m_A in the definition of the mean speed by $\mu_{A,B}$, the *reduced mass* for the A,B pair. The reduced mass is defined as:

$$\mu_{A,B} \equiv \frac{m_A m_B}{m_A + m_B}, \text{ or equivalently, } \frac{1}{\mu_{A,B}} \equiv \frac{1}{m_A} + \frac{1}{m_B}. \tag{6.10}$$

If $m_B \gg m_A$, $\mu_{A,B} \approx m_A$, i.e., the mass of the lighter species, while if $A = B$, $\mu_{A,A} = m_A/2$.

With this correction, our expression becomes

$$Z_{A,B} = \pi(R_A + R_B)^2 \langle c_{A,B} \rangle n_A n_B, \tag{6.11}$$

where

$$\langle c_{A,B} \rangle \equiv \left(\frac{8k_BT}{\pi \mu_{A,B}} \right)^{1/2}, \tag{6.12}$$

is the mean speed of A relative to B. A special case of this expression it the rate of collision of A molecules with themselves. In this case, Eq. (6.11) becomes

$$Z_{A,A} = \frac{1}{2} \pi \sigma_A^2 \langle c_A \rangle 2^{1/2} n_A^2, \tag{6.13}$$

where $\sigma_A = 2R_A$ is the molecular diameter of A and where we have divided by 2 in order to not count each A-A collision twice. Note that we have expressed our result in terms of $\langle c_A \rangle$ and not $\langle c_{A,A} \rangle$, which is the origin of the additional factor of $2^{1/2}$ in Eq. (6.13).

Equations (6.11) or (6.13) give the rate of chemical reaction per unit volume, *assuming zero activation energy* (this is still an upper bound to the rate of reaction). As in the collision with a wall discussion, this is easily generalized by including in the collision rate only those molecules with enough (relative) kinetic energy; i.e.,

$$RATE = n_A n_B \pi (R_A + R_B)^2 \int_{c_{\min}}^{\infty} dc\, F(c) c = \pi(R_A + R_B)^2 \langle c_{A,B} \rangle e^{-E_A/k_BT} \left(1 + \frac{E_A}{k_BT} \right) n_A n_B, \tag{6.14}$$

where $F(c)$ is the (relative) speed distribution and $E_A \equiv \mu_{A,B} c_{\min}^2/2$. When A=B we have to add the additional factor of 1/2, cf. Eq. (6.13).

This expression has the correct Arrhenius form except for the extra non-exponential factors containing temperature. However, compared with the exponential factor, these usually do not change very rapidly with temperature and can approximately be treated as constant; recall that we normally show Arrhenius behavior by plotting ln(Rate Constant) versus $1/T$ to obtain a straight line. The non-exponential terms end up in a logarithm which usually doesn't change much over the range of temperatures studied. Thus, we have derived an approximate expression for the bi-molecular rate constant which has at least some of the qualitative features of those found in gas reactions. Note that in either case we have a second order reaction overall, either first order in A and first order in B or second order in A, cf. Eq. (6.14) or, ignoring any activation energy, (6.13), respectively.

It is important to understand what we mean by 'RATE' in Eq. (6.14). It is the average number of reactive collisions per unit volume, per unit time. This need not be the rate of disappearance of reactants or appearance of products per unit time per unit volume. To get these we need the stochiometries in the reaction under consideration. Consider the following reaction

$$A + A \to A_2. \tag{6.15}$$

In each reactive collision two A's are consumed, while only one A_2 is produced; thus the rate of disappearance of A is twice the rate of appearance of A_2, which in turn happens once per event. Hence,

$$\frac{d[A_2]}{dt} = RATE, \quad \text{while} \quad \frac{d[A]}{dt} = -2 \times RATE. \tag{6.16}$$

Note that Eq. (6.16) implies that $[A] + 2[A_2]$ is constant. Why should this not be a surprise?

6.3. Mean Free Path and Transport Phenomena

Next, we will consider how far a molecule can move before it suffers a collision. For simplicity, we will only consider a one component gas. According to Eq. (6.7), the mean time between collisions is

$$\tau_{collision} \approx \frac{1}{Z_{A \text{ with } A's}} = \frac{1}{2^{1/2}\pi\sigma_A^2 \langle c_A \rangle n_A}, \tag{6.17}$$

where $\sigma_A = 2R_A$ is the diameter of and A. Hence, the typical distance traveled by a molecule between collisions, λ is approximately $\tau_{collision}\langle c_A \rangle$ or

$$\lambda = \frac{1}{2^{1/2}\pi\sigma_A^2 n_A}. \tag{6.18}$$

This distance is called the mean free path. Note that it only depends on the number density of the gas and the size of the molecules, but not its mass or the temperature.

We can use these results to obtain an approximate expression for the way in which concentration differences equilibrate in a dilute gas. Consider a gas containing two kinds of molecules in which there is a concentration gradient; i.e., the density of molecules per unit volume, $n_i(z)$ depends on position. One way in which the concentration becomes uniform is via diffusion.

To quantify diffusion, we want to find the net number of molecules of a given type that cross a plane in the gas per unit area per unit time; this is known as the diffusion flux. To see how the diffusion flux depends on molecular parameters, consider the following figure.

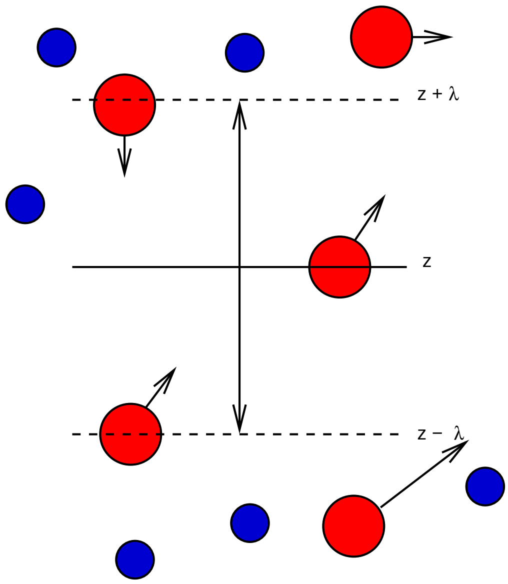


Fig. 6.2. Any molecule that starts around a mean free path from the mid-plane will not collide with anything and will cross the mid-plane, therefore contributing to the upward or downward flux. The net rate per unit area is just what we considered in our discussion of effusion.

We want the net flux through the plane at z. From our preceding discussion of mean free paths, clearly any molecule that starts roughly from a mean free path above or below z, moving towards z, will not suffer any collisions and will cross. The number that cross the planes at $z \pm \lambda$ per unit area, per unit time is the same as the wall collision rates we calculated above, that is

$$\left(\frac{k_B T}{2\pi m}\right)^{1/2} n(z \pm \lambda) = \frac{1}{4}\langle c_A \rangle n(z \pm \lambda), \tag{6.19}$$

where we have rewritten Eq. (6.3) in terms of the average molecular speed, cf. Eq. (6.8). Since all the molecules that won't collide and will thus cross the plane at z, the net flux (upward) is just

$$J = \frac{1}{4}\langle c_A \rangle n(z-\lambda) - \frac{1}{4}\langle c \rangle n(z+\lambda) = -\frac{1}{4}\langle c_A \rangle [n(z+\lambda) - n(z-\lambda)]. \tag{6.20}$$

Since, for most experiments the density barely changes on over a distance comparable to the mean free path, we use the Taylor expansion to write

$$n(z \pm \lambda) \approx n(z) \pm \frac{dn(z)}{dz}\lambda + \frac{1}{2}\frac{d^2 n(z)}{dz^2}\lambda^2 + \cdots, \tag{6.21}$$

which, when used in Eq. (6.20) gives Fick's First Law of diffusion,

$$J = -D\left(\frac{\partial n(z,t)}{\partial z}\right)_t \tag{6.22}$$

where we have modified the notation to include the time dependence of the density and where

$$D \equiv \frac{1}{2}\,\lambda\langle c_A\rangle. \tag{6.23}$$

D is known as the diffusion constant and has units of $length^2/time$.

The factor of 1/2 in our expression for D is not quite right, but the other factors are; e.g., for hard spheres the correct diffusion constant is $3\pi/8 = 1.178\ldots$ times larger than the one given above.* Note that only the leading order term was kept in obtaining Eqs. (6.22) and (6.23) from Eqs. (6.20) and (6.21); the next order one contains $\lambda^3(\partial^3 n(z,t)/\partial z^3)_t$, and in general, only odd powers of λ and numbers of derivatives will appear.

Next consider the total number of molecules inside of some region bounded by planes at z and $z+L$. The length L is small compared to the scales that characterize the concentration nonuniformity, but large compared with the mean free path. Clearly the only way for the total number of molecules in our region, $n(z,t)L$, to change is by fluxes at the surfaces at z and $z+L$. Thus,

$$\frac{\partial n(z,t)L}{\partial t} = -J(z+L,t) + J(z,t) \approx -L\,\frac{\partial J(z,t)}{\partial z}\,, \tag{6.24}$$

where we have again used a Taylor expansion, now for the flux itself. Finally, by using our result for the diffusion flux and canceling the factors of L, we see that

$$\left(\frac{\partial n(z,t)}{\partial t}\right)_z = D\left(\frac{\partial^2 n(z,t)}{\partial z^2}\right)_t, \tag{6.25}$$

which is a kinetic equation for the relaxation of the concentration and is known as the diffusion equation. Although value of the diffusion constant is quite different, the diffusion equation actually is more general than our derivation might suggest and holds in liquids and solids as well. Finally, note that we have only considered systems where the concentration is only nonuniform in one spatial direction. Should this not be the case, then some simple modifications of our expressions must be introduced, but these will not be considered here.

There are standard ways in which to solve diffusion equations, either analytically, for special geometries, or numerically.† However, there is one general feature of systems relaxing diffusively. Imagine introducing a small droplet of an impurity into a system. Clearly the droplet will spread in time, and you might naively think that the average droplet size would grow like $\langle c_A\rangle t$. Of course, this ignores collisions and is incorrect. From the diffusion equation dimensional

*See, e.g., Joseph O. Hirschfelder, Charles F. Curtiss, R. Byron Bird, *Molecular Theory of Gases and Liquids* (Wiley-Interscience, 1964), Chapters 7-8. Be warned, the math and physics required is very non-trivial!

†See, e.g., W.H. Press, S.A Teukolsky, W.T. Vetterling, and B.P. Flannery, *Numerical Recipes in C: The Art of Scientific Computing*, 2nd ed., (Cambridge University Press, 1992), Ch. 19.

analysis correctly suggests that

$$\frac{1}{t} \approx \frac{D}{R^2} \tag{6.26}$$

or $R \approx \sqrt{Dt}$, which is much slower than the linear time behavior that would arise in the absence of collisions.‡ This is what is observed.

The preceding analysis can be applied to other transport phenomena; in particular to energy or momentum transport. One interesting example is to so-called transport of shear momentum. Consider a flowing system with velocity in the x direction and gradient in the z direction, or

$$\mathbf{v}(\mathbf{r}) = \hat{\mathbf{e}}_x \mathrm{v}(z). \tag{6.27}$$

For linear profiles we have a Couette flow, for parabolic ones a Poiseuille flow, etc. The momentum per unit volume (or momentum density) is just $\hat{\mathbf{e}}_x mn\mathrm{v}(z)$ Repeating our analysis of Fig. 2, but now for the flux for the x component of the momentum being transported in the z direction, denoted as $\tau_{x,y}$, gives

$$\tau_{x,y} = -\frac{1}{4}\langle c_A\rangle mn[\mathrm{v}(z+\lambda) - \mathrm{v}(z-\lambda)] \approx -\frac{\lambda}{2}\langle c_A\rangle mn\left(\frac{\partial \mathrm{v}}{\partial z}\right) \equiv -\eta\left(\frac{\partial \mathrm{v}}{\partial z}\right), \tag{6.28}$$

where $\eta \equiv \lambda\langle c_A\rangle mn/2$ is known as the dynamic viscosity. (Again, like the diffusion coefficient, the factor of 2 isn't quite right, but the rest is.)

If we repeat the steps leading to the diffusion equation, we find that

$$\left(\frac{\partial \mathrm{v}_x(z,t)}{\partial t}\right)_z = \nu\left(\frac{\partial^2 \mathrm{v}_x(z,t)}{\partial z^2}\right)_t, \tag{6.29}$$

where $\nu \equiv \eta/mn$ is known as the kinematic viscosity and has units of *length*^{2}/*time*. Note that $\nu = D$ in our treatment, but this is an accidental consequence of our model (the factors of 2 aren't quite right). This last equation is a special case of the Navier-Stokes equations (in particular, we have ignored the role of pressure in directly exerting a force on the molecules, thereby changing the momentum).

6.4. Appendix: The Center of Mass Frame

Here are the details of the center of mass calculation mentioned in the text. (**You are not responsible for these details**). Consider two particles with masses m_i, at positions $\mathbf{r}_i$, moving with velocities $\mathbf{v}_i$, $i = 1, 2$. The center of mass for this system is given by

$$\mathbf{R}_{cm} \equiv \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2}\ . \tag{A.1}$$

Also define the relative coordinate for the pair as

‡ For a spherical droplet the exact answer is $R = \sqrt{6Dt}$.

$$\mathbf{r}_{12} \equiv \mathbf{r}_1 - \mathbf{r}_{2.} \tag{A.2}$$

Similar definitions hold for the center of mass and relative velocities. A little algebra allows us to express the original coordinates in terms of the center of mass and relative ones; namely,

$$\mathbf{r}_1 = \mathbf{R}_{cm} + \frac{m_2}{m_1 + m_2}\mathbf{r}_{12} \tag{A.3a}$$

and

$$\mathbf{r}_2 = \mathbf{R}_{cm} - \frac{m_1}{m_1 + m_2}\mathbf{r}_{12}, \tag{A.3b}$$

where, again, similar expressions are obtained relating the velocities.

Now consider the probability densities for finding particle 1 at velocity $\mathbf{v}_1$ and 2 at velocity $\mathbf{v}_2$:

$$f(\mathbf{v}_1, \mathbf{v}_2) = \left(\frac{m_1 m_2}{(2\pi k_B T)^2}\right)^{3/2} \exp\left(-\frac{m_1 v_1^2 + m_2 v_2^2}{2k_B T}\right) \tag{A.4a}$$

$$= \left(\frac{(m_1 + m_{2)}\mu}{(2\pi k_B T)^2}\right)^{3/2} \exp\left(-\frac{(m_1 + m_2)V_{cm}^2 + \mu v_{12}^2}{2k_B T}\right)$$

$$= \left(\frac{(m_1 + m_{2)}}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{(m_1 + m_2)V_{cm}^2}{2k_B T}\right)\left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{\mu v_{12}^2}{2k_B T}\right)$$

$$\equiv \qquad f_{cm}(\mathbf{V}_{cm}) \qquad \times \qquad f_{12}(\mathbf{v}_{12}), \tag{A.4b}$$

where the second equality is obtained by expressing the individual velocities in terms of the center of mass and relative velocities, cf. Eqs. (A.3a) and (A.3b), with μ given by Eq. (6.10). The third equality is obtained by splitting up the exponentials and the factors in front, and finally, the last equality is obtained by defining the center of mass or relative velocity distributions as usual, but with the masses replaced by the total mass or reduced mass, respectively.

Thus, we've shown that the probability densities for the two particles' center of mass and relative velocities factorize; i.e., they are statistically independent. (Strictly speaking we have to check one more thing, namely, that $d\mathbf{v}_1 d\mathbf{v}_2 = d\mathbf{V}_{cm} d\mathbf{v}_{12}$. This is easily done by showing that the Jacobian for the transformation, cf. Eqs. (A.3a) and (A.3b), is unity, which it is. Jacobians are a Cal III concept). In any event, Eq. (A.4b) shows that any question that only asks about the relative motion of the particles (e.g., as in a collision) can ignore the center of mass part completely, and as was mentioned in the main text, in practice means that we replace the mass by the reduced mass in the distribution.

7. Work, Heat, and Energy

7.1. Zeroth Law of Thermodynamics

> If two bodies at equilibrium are brought into *thermal* contact (i.e., no mechanical, electrical, magnetic, gravitational, etc., work is performed) and **nothing** happens, then they are at the same temperature.

Given this, we can always measure the temperature of any system by bringing it into thermal contact with some standard thermometer. As we shall see, a very convenient choice is the ideal-gas thermometer. Here a manometer is used to measure the pressure of a fixed amount of gas in a fixed volume and the relation

$$P = \frac{NRT}{V}$$

is used to calculate the temperature. Needless to say, other temperature standards can (and are) used.

7.2. Some Definitions

Intensive: Doesn't depend on the size of the system; e.g., P, T, partial molar quantities.

Extensive: The opposite of intensive; e.g., mass, volume, energy (but not energy per unit volume or mass), heat capacities (but not specific heats).

System: The part of the universe under investigation. Systems can be:

a) Isolated: no interaction of any kind with surroundings. Note that real systems cannot be truly isolated, but can be approximately so on the time-scale of relevance.

b) Closed: energy can be exchanged with surroundings, but matter cannot.

c) Open: matter and energy can be exchanged.

Surroundings: The part of the universe not under investigation.

Boundary: What divides the system from the surroundings (and controls whether the system is open, closed, or isolated).

State: A systems state is specified when all measurable properties have definite values *to the accuracy of the experiment*.

State Variables: A set of measurable quantities, which when known, completely specify the state of the system. In classical or quantum mechanics there are on the order of 10^{23} state variables; however, in thermodynamics, experience tells us that the **macroscopic** state of the system is specified after a small set of measurements are made (e.g., T, P, V, $x_1, \ldots, x_r$).

Process: Something whereby the state of a system is changed. A process has two parts:

a) Initial and final states (i.e., where the system starts and ends).

b) A Path. The path describes how the change was effected. In order to specify the path, intermediate changes in the system, surroundings and boundary must be specified. This is clearly something which we would like to avoid in many cases.

Reversible A process is said to be reversible if it is possible to return **both** the system and the surroundings to their original state. If not, it is irreversible (even if the system can be returned to the original state).

State Function A property of the system which only depends on the current state of the system. Hence, changes in state functions do not depend on the path taken. State functions play a key role in thermodynamics and allow macroscopic properties of matter to be studied in a rigorous, systematic manner. Examples of state functions are: energy, entropy (to be introduced later), P, V, T, etc. A one-component ideal gas has a pressure, P(T,N,V), given by PV=NRT no matter what--how the T, V, or N attained their current values is irrelevant.

7.3. Euler's Theorem, Partial Molar Quantities, and the Gibbs-Duhem Relations

Next consider any extensive quantity in a mixture containing r components; i.e., $A(T, P, N_1, \ldots, N_r)$. Real examples could be the energy, volume, mass, heat capacity, etc.. Consider the small change in A associated with changes in its arguments, namely*

$$dA = \left(\frac{\partial A}{\partial T}\right)_{P,N_1,\ldots,N_r} dT + \left(\frac{\partial A}{\partial P}\right)_{T,N_1,\ldots,N_r} dP + \left(\frac{\partial A}{\partial N_1}\right)_{T,P,N_2,\ldots,N_r} dN_1 + \ldots + \left(\frac{\partial A}{\partial N_r}\right)_{T,P,N_1,\ldots,N_{r-1}} dN_r. \tag{7.1}$$

Now, by assumption, A is extensive; hence,

$$\lambda A(T, P, N_1, \ldots, N_r) = A(T, P, \lambda N_1, \ldots, \lambda N_r). \tag{7.2}$$

If we differentiate both sides of this equation with respect to λ and evaluate the result at $\lambda = 1$ it follows that

$$A(T, P, N_1, \ldots, N_r) = \left(\frac{\partial A}{\partial N_1}\right)_{T,P,N_2,\ldots,N_r} N_1 + \ldots + \left(\frac{\partial A}{\partial N_r}\right)_{T,P,N_1,\ldots,N_{r-1}} N_r \tag{7.3}$$

$$\equiv \sum_{i=1}^{r} \bar{A}_i N_i, \tag{7.4}$$

where

$$\bar{A}_i \equiv \left(\frac{\partial A}{\partial N_i}\right)_{T,P,N_{j\neq i}} \tag{7.5}$$

is called a *partial molar quantity*. Note that the partial molar quantities are intensive. In obtaining Eq. (7.3) you may use Eq. (7.1) for $dT = dP = dN_i = 0$ and $d(\lambda N_i) = N_i d\lambda$ for $i = 1, \ldots, r$). Also note that Eq. (7.3) is a special case of Euler's theorem for homogeneous functions in calculus.

Equations (7.3) or (7.4) allow us to explicitly express the nontrivial features of an extensive quantity in terms of intensive ones, thereby reducing the number of dependencies we must worry about. It also turns out that the partial molar quantities (or more specifically, changes in

*Note that we may use Eq. (7.1) to work out what is known as a total derivative. Consider the case where $r = 1$, i.e., $N_1 = N(T, P)$. We'll keep P constant and consider the remaining N be a function of T and P. By dividing Eq. (7.1) by dT it follows that

$$\left(\frac{dA}{dT}\right)_P = \left(\frac{\partial A}{\partial T}\right)_{P,N} + \left(\frac{\partial A}{\partial N}\right)_{T,P}\left(\frac{\partial N}{\partial T}\right)_P.$$

Note that the first term on the right hand side is just the usual derivative while the second is an example of the chain rule.

them) are not all independent. To see this, we calculate dA from Eq. (7.4):

$$dA = \sum_{i=1}^{r} \bar{A}_i dN_i + N_i d\bar{A}_i, \tag{7.6}$$

where we have used the calculus result $d(xy) = xdy + ydx$. Of course, dA could have been computed from Eq. (7.1); i.e.,

$$dA = \left(\frac{\partial A}{\partial T}\right)_{P,N_1,\ldots,N_r} dT + \left(\frac{\partial A}{\partial P}\right)_{T,N_1,\ldots,N_r} dP + \sum_{i=1}^{r} \bar{A}_i dN_i, \tag{7.7}$$

where we have rewritten the derivatives with respect to the numbers of moles in terms of the partial molar quantities, cf. Eq. (7.5). By equating the right hand sides of Eqs. (7.6) and (7.7) it follows that

$$\left(\frac{\partial A}{\partial T}\right)_{P,N_1,\ldots,N_r} dT + \left(\frac{\partial A}{\partial P}\right)_{T,N_1,\ldots,N_r} dP - \sum_{i=1}^{r} N_i d\bar{A}_i = 0, \tag{7.8}$$

and hence, the changes in the partial molar quantities and other derivatives are not all independent. Equation (8) is known as a Gibbs-Duhem relation and can be used to relate seemingly disparate thermodynamic derivatives.

As an exercise, what are the partial molar volumes for an ideal gas mixture obeying Dalton's law of partial pressures? Do they obey the Gibbs-Duhem relation?

7.4. Work and Heat in Thermodynamics

Two central concepts in thermodynamics are work and heat. You probably have seen examples of the former in your freshman physics class, and the latter is something you experience in daily life. In thermodynamics, both have very precise definitions.

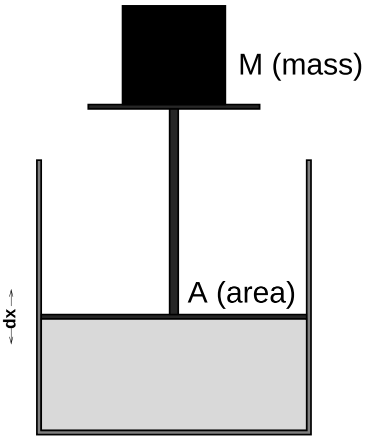
Work: Anything which crosses the boundary of the system and is completely convertible into the lifting of a weight in the surroundings.

Note that work only appears at the boundary of a system, during a change of state, is extensive, and is manifested by an effect in the surroundings. From mechanics, we know that

$$dW = Fdx = -mgdx, \tag{7.9}$$

where dW is the incremental work done, F is the force being exerted on the system, and dx is the distance traversed. The second equality is for moving a mass m a distance dx in a gravitational field (g is the gravitational acceleration constant). Note that there are two sign conventions for work in thermodynamics. In the older, the force is that exerted by the system on the surroundings, and the corresponding work is the work done by the system on the surroundings. In the newer convention, things are reversed; the force is the force the surroundings exert on the system and the work is that done by the surroundings on the system. Since Newton's law states that these two forces must be equal and opposite, the two conventions differ by a sign. The text, and we, will use the latter convention here although note that Castellan uses the older convention.

Consider the following apparatus:



The inside of the piston is filled with some gas at pressure P and is maintained at constant temperature T. Instead of characterizing the work done in terms of the mass, it is more convenient to introduce the pressure exerted on the top of the piston (i.e., force per unit area, A)

$$P_{op} \equiv \frac{F}{A} = \frac{mg}{A}, \tag{7.10}$$

and acts downward. Note that P_{op} need not equal P.

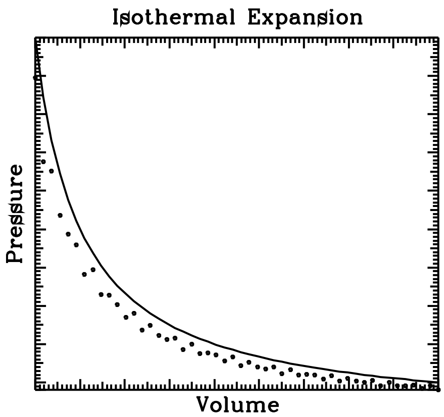
Thus

$$đ W = -P_{op} A dx = -P_{op} dV, \tag{7.11}$$

where dV is the incremental change in the volume of the system. The work involved in these sorts of processes is known as pressure-volume work.

Note that the work done is **not** a state function--it depends on the pressure exerted on the piston (the path) and is not simply a function of the state of the gas in the piston. To stress this fact, the notation $đ$ will be used for infinitesimal changes in quantities which depend on the path.

For an process whereby the gas is expanded against some pressure, $dV > 0$, and hence, $đ W < 0$. Conversely, in a compression process, $đ W > 0$, i.e., negative work is done by the system. The surroundings do positive work on the system.



This diagram shows a process for the isothermal expansion of a gas (in this case an ideal gas). The solid curve gives the pressure of the gas (i.e., its equation of state). The dotted curve gives the opposing pressure actually used in the expansion. Note that the latter lies completely below the former. If at any point this were not the case, then the expansion would not proceed spontaneously (i.e., the opposing pressure would be too large and the gas would contract).

The total work done by the surroundings on the system (- the total work done by the system on surroundings) is just the negative of the area under the dotted curve:

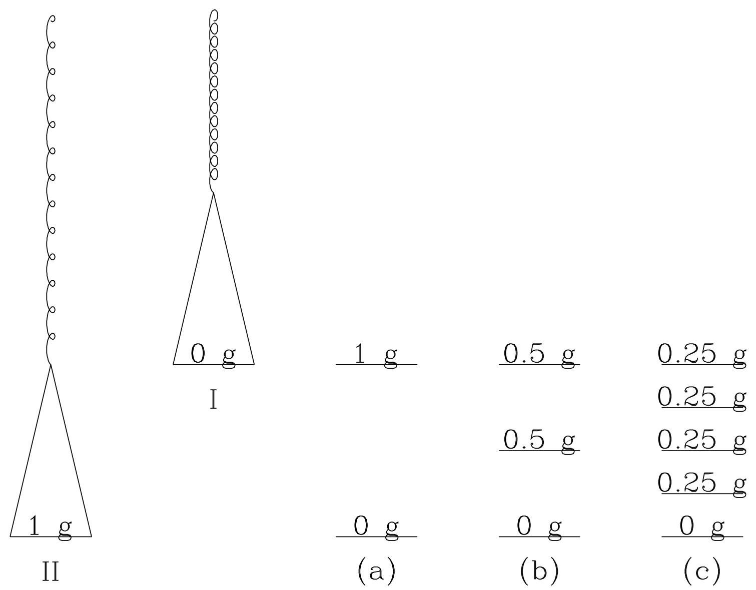
$$W = -\int_{V_{initial}}^{V_{final}} P_{op}(V) dV \geq -\int_{V_{initial}}^{V_{final}} P(V) dV \equiv W_{rev}. \tag{7.12}$$

If the gas inside the piston is ideal, then the ideal-gas equation of state is valid and

$$W_{rev} = -\int_{V_{initial}}^{V_{final}} \frac{NRT}{V} dV = -NRT \ln(V_{final}/V_{initial}). \tag{7.13}$$

Note that the maximum work you can get out of a spontaneous expansion is obtained when the opposing pressure is infinitesimally less than the pressure being exerted by the gas in the piston. In this case, $W = W_R$. Unfortunately, the rate of such an expansion would be zero, as would be the power delivered by the system. On the other hand, it is easy to show that the path given by $P_{op} = P$ is the only reversible one for the isothermal expansion of an ideal gas.

Consider the following apparatus (from L. K. Nash, *Elements of Chemical Thermodynamics*, Addison-Wesley, 1970):



The spring is assumed to obey Hooke's law (i.e, the force is proportional to the elongation). A series of experiments are performed whereby weights are moved to pan from platforms at various heights in the surroundings. In doing so, the system (the spring and pan) move from state I to II. How much work is performed in each of the cases (a)–(c) (assume that there is a total 1cm elongation of the spring and ignore the mass of the pan and spring)?

In order to reverse the process (i.e., the expansion of the spring) the weights are moved back to the adjacent platforms. However, it is easy to see that while the spring will be fully compressed at the end of the experiment, the surroundings will not be restored to their initial state; specifically, in the best case, the topmost weight will be transferred to the lowest platform, no matter how many platforms are used. Clearly the biggest change in the surroundings will happen in case (a) and the smallest in (c). Moreover, the smaller the individual weights we use, the more reversible the process becomes (i.e., the change to the surroundings decreases). The process is reversible in the limit where the applied force (the weight) is only infinitesimally more than the force exerted by the spring.

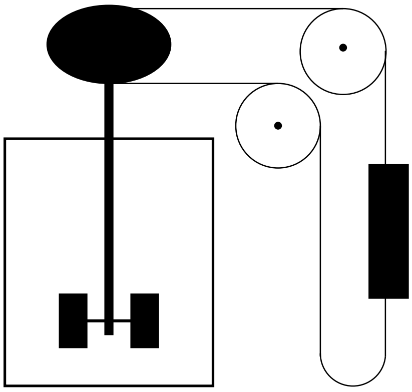
This argument can easily be extended to our discussion of pressure-volume work or to other kinds of work. Hence, the maximum work in a P-V expansion is obtained for a reversible path.

Another key quantity in thermodynamics is heat.

Heat: Anything which flows across the boundary of a system by virtue of a temperature difference between the system and the surroundings.

Heat is quantified by measuring the temperature rise (or fall) in a standard material (e.g., a calorie corresponds to the amount of heat required to raise the temperature of 1 g of water 1 ^{0}C). Like work, heat appears only at the boundary of a system, during a change of state, is extensive, and is manifested by an effect in the surroundings. It is also not a state function since it depends on the nature of the thermal contact allowed at the boundary of the system.

In a classic set of experiments in the 19'th century, J. P. Joule showed that the same changes in the state of a system could be achieved by either adding work or heat to the system. One of his devices is shown below.



As the weight falls, the paddles turn and heat up the liquid in the container by friction (viscous heating). The same temperature rise can be achieved by directly heating the container using a known amount of heat.

The amounts of heat and work were definite and Joule concluded that work and heat were simply two different ways in which energy could be added to a system. Specifically, Joule showed that

$$1\ calorie = 4.184\ kg\ m^2/sec^2.$$

We are now ready to state the first law of thermodynamics.

7.5. The First Law of Thermodynamics:

In any cyclic process (i.e., one where the system returns to its initial state) the net heat absorbed by the system is equal to the work produced by the system.

Suppose this were not the case. Then you could presumably find a process which produced more work than it absorbed heat. This extra work could be used to run a generator, which in turn could be used to produce more heat, which could run more of the process, producing even more excess work, and so on. The energy crisis, electric bills, etc. would be things of the past. Unfortunately, no such device has ever been built and the first law still stands.

In mathematical terms, the first law implies that there is a state function, called the internal energy of the system, defined up to an arbitrary additive constant through its differential

$$dE \equiv đQ + đW, \tag{7.14}$$

where $đW$ is the work done by the surroundings on the system (the negative of the work done by the system on the surroundings). For a finite change of state, the change in the internal energy, ΔE, is given by

$$\Delta E = \int_{initial\ state}^{final\ state} đQ + đW. \tag{7.15}$$

The first law states that

$$\oint dE = \oint đQ + \oint đW = 0. \tag{7.16}$$

The first law implies that the energy change computed along different paths must give the same answer. If not, two such paths could be used to to build the energy-creating device discussed above (i.e., by reversing one of the paths). The appendix contains a detailed discussion of the conservation of energy in (classical) mechanics; as expected there the discussion revolves around forces, which while similar to the discussion of $đW$ in special cases, leaves the connection to heat and $đQ$ somewhat obscure.

7.6. Some Properties of the Energy

In order to calculate or measure energies, we note that $đW = 0$ for constant volume systems, assuming that only pressure-volume work can be done. Hence, $dE = dQ_V$, where we have dropped the $đ$ in favor of d and have put a "V" subscript on the Q to emphasize that we are working at constant volume. (Why is this valid?). In the absence of phase changes (e.g., vaporization), the increments of heat absorbed by the system are proportional to the incremental temperature change of the system; i.e.,

$$dE = dQ_V = C_V dT, \tag{7.17}$$

were $C_V \equiv \left(\frac{\partial E}{\partial T}\right)_{V,N}$ is known as the constant volume heat capacity and in general is an extensive property of the system that depends on T, P, composition and phase, and is positive in general. Since $E = \frac{3}{2} NRT$ for an ideal gas of point particles, it follows that $C_V = \frac{3}{2} NR$. By integrating both sides of the equation we find that

$$\Delta E_{T_i \to T_f} = Q_V = \int_{T_i}^{T_f} C_V(T, V, N) dT. \tag{7.18}$$

Note that ΔE is positive for an endothermic constant volume process and is negative for an exothermic one. If there is a phase change during the experiment, we have to add the latent energy change of the phase transition (i.e., the heat we would have to add at the transition temperature to convert all the material from one phase to another) to the right hand side of our expression.

Thus, we have found a simple situation in which the energy change is related to heat. Unfortunately, the requirement of constant volume, while realizable to high accuracy in the lab, is inconvenient. Is there another quantity that becomes the heat absorbed by the system under other conditions, and in particular for constant pressure? In fact there is and a simply trick allows us to find it.

Consider the quantity $H \equiv E + PV$, known as the Enthalpy. Since E and PV are state functions, so too is H. Next, by taking the differential of each side of the definition and using the

First Law, we find that

$$dH = dE + PdV + VdP = đQ + (P - P_{op})dV + VdP, \tag{7.19}$$

where only pressure-volume work has been allowed; i.e., $đW = -P_{op}dV$. As we discussed above, for reversible changes, $P_{op} = P$ and

$$dH = dQ + VdP \tag{7.20}$$

For processes where the pressure is constant, $P_{op} = P$ and $dP = 0$, which gives

$$dH = dQ_P = C_P dT \tag{7.21}$$

where, $C_P \equiv \left(\frac{\partial H}{\partial T}\right)_{P,N}$ is the constant pressure heat capacity. For the ideal gas, $H = E + PV = \frac{5}{2}NRT$, and thus, $C_P = \frac{5}{2}NR$. Note that $C_P > C_V$, something that is true more generally. Finally, by repeating the discussion we had for the energy, it follows that

$$\Delta H = Q_P = \int_{T_i}^{T_f} C_P(T, P, N)dT, \tag{7.22}$$

again with extra terms to account for the latent enthalpy (heat) of transition(s) should phase changes occur. This procedure is known as a Legendre transformation, and we will see other applications of it later.

7.7. Appendix: Energy in Classical Mechanics

You probably have heard the statement "energy is conserved." What does this mean exactly? Consider a system comprised of N point particles of mass m, at positions $\mathbf{r}_1, \ldots, \mathbf{r}_N$, and moving with velocities $\mathbf{v}_1, \ldots, \mathbf{v}_N$. The system is subjected to external forces described by a time dependent potential $\phi_{ext}(\mathbf{r}, t)$, e.g., as might arise from the interaction of the molecules in the system with a moving piston, or with the atoms in the bottom of a container being heated from below. In addition, assume that Newton's laws of motion are valid and that the particles interact via pairwise additive forces which are derivable from a potential; i.e., the force particle j exerts on i, $\mathbf{F}_{i,j}$ is given by

$$\mathbf{F}_{i,j} \equiv -\frac{\partial u_{i,j}}{\partial \mathbf{r}_i}, \tag{7.23}$$

where $u_{i,j}$ is the potential energy of interaction between molecules i and j and depends on the molecular positions through $\mathbf{r}_i - \mathbf{r}_j$ (i.e., only through the separation between the molecules).

Consider the mechanical energy, E, defined as

$$E \equiv \sum_{i=1}^{N} \frac{m}{2}\mathbf{v}_i^2 + \frac{1}{2}\sum_{\substack{i=1 \\ i\neq j}}^{N}\sum_{j=1}^{N} u_{i,j} + \sum_{i=1}^{N}\phi_{ext}(\mathbf{r}_i, t). \tag{7.24}$$

Note that the last term describes the interaction between the system and its surroundings, and the internal energy would drop this term in its definition. How does E change as the particles move around under the action of Newton's Laws?

$$\frac{dE}{dt} = \sum_{i=1}^{N} \mathbf{v}_i \cdot \mathbf{F}_i - \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ i \neq j}}^{N} \mathbf{F}_{i,j} \cdot (\mathbf{v}_i - \mathbf{v}_j) + \sum_{i=1}^{N} \left[\left(\frac{\partial \phi_{ext}(\mathbf{r}_i, t)}{\partial t} \right)_{\mathbf{r}_i} - \mathbf{v}_i \cdot \mathbf{F}_{ext}(\mathbf{r}_i, t) \right] \tag{7.25}$$

where $\mathbf{F}_{ext}(\mathbf{r},t) \equiv -(\partial \phi_{ext}(\mathbf{r}, t)/\partial \mathbf{r})_t$, is the external force, and $\mathbf{F}_i \equiv \sum_{j \neq i} \mathbf{F}_{i,j} + \mathbf{F}_{ext}(\mathbf{r}_i, t)$, is the total force acting on the i'th particle. By using this expression for $\mathbf{F}_i$ in the rate of change of E we find that

$$\frac{dE}{dt} = \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ i \neq j}}^{N} \mathbf{F}_{i,j} \cdot (\mathbf{v}_i + \mathbf{v}_j) + \sum_{i=1}^{N} \left(\frac{\partial \phi_{ext}(\mathbf{r}_i, t)}{\partial t} \right)_{\mathbf{r}_i} = \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ i \neq j}}^{N} (\mathbf{F}_{i,j} + \mathbf{F}_{j,i}) \cdot \mathbf{v}_i + \sum_{i=1}^{N} \left(\frac{\partial \phi_{ext}(\mathbf{r}_i, t)}{\partial t} \right)_{\mathbf{r}_i} \tag{7.26}$$

where the dummy summation indices, i and j, were exchanged for the terms in $\mathbf{v}_j$ in obtaining the last equality. Newton's third law states that $\mathbf{F}_{i,j} = -\mathbf{F}_{j,i}$; i.e., the force i exerts on j is equal in magnitude and opposite in direction to that j exerts on i. Using this in our last expression immediately shows that

$$\frac{dE}{dt} = \sum_{i=1}^{N} \left(\frac{\partial \phi_{ext}(\mathbf{r}_i, t)}{\partial t} \right)_{\mathbf{r}_i}. \tag{7.27}$$

In other words, in the absence of *explicitly time-dependent* external forces, the energy of our classical system of particles doesn't change in time i.e., it is conserved. The same is true under the laws of quantum mechanics.

Finally, note that our result is dependent on our definition of the energy. For example, if we consider the so-called internal energy, i.e.,

$$E_{int} \equiv \sum_{i=1}^{N} \frac{m}{2} \mathbf{v}_i^2 + \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ i \neq j}}^{N} u_{i,j}, \tag{7.28}$$

cf. Eq. (7.24), and repeat the steps leading to Eq. (7.27), it follows that

$$\frac{dE_{int}}{dt} = \sum_{i=1}^{N} \mathbf{v}_i \cdot \mathbf{F}_{ext}(\mathbf{r}_i, t), \tag{7.29}$$

which is essentially the result we obtain by starting with $đW = \mathbf{F} \cdot d\mathbf{r}$.

The first law of thermodynamics also has something to say about changes in energy, although not in precisely the same way as in classical or quantum mechanics. Specifically, where are work and heat, and is our expression for the energy (or internal energy) a state function? Indeed, all that appears the rate of change of the internal energy, cf. Eq. (7.29), are forces acting on the full many-body system; no distinction is made between heat, mechanical work, etc., and which while certainly correct, leaves one wondering where to find the practical simplifications the thermodynamic approach gives.

8. Thermochemistry

8.1. Enthalpy Calculations: Chemical Reactions and Hess' Law

The enthalpy change for a process, ΔH, is equal to the heat absorbed by the system if that process is done under constant pressure conditions (and assuming that only P-V work is possible). Since the enthalpy of a system, H = E + PV, is a state function, we can systematize enthalpy calculations by considering a path whereby the compounds first turn into their constituent elements in their standard states (by convention at 25 ^{o}C and 1 atm pressure) and then recombine to form the products. The enthalpy change in the latter step is just the enthalpy of formation of the products and the former is the enthalpy of destruction (i.e., the negative of the enthalpy of formation) of the reactants. Hence,

$$\Delta H = \sum \left[\Delta H_f^0(products) - \Delta H_f^0(reactants) \right]. \tag{8.1}$$

Since we are interested in calculating a difference, the absolute enthalpy of the elements in their standard states is unimportant [it cancels out of Eq. (8.1)], and we adopt the convention that the enthalpy of formation of an element in its standard state is zero.

Consider the following example (reduction of iron oxide):

$$Fe_2O_3(s) + 3H_2(g) \overset{25\ ^oC,\ 1\ \mathrm{atm}}{\rightarrow} 2Fe(s) + 3H_2O(l). \tag{8.2}$$

A table of thermochemical data gives:

Enthalpies of Formation at 1 atm and 25 C

Compound	ΔH_f^0 (kJ/mol)
Fe_2O_3(s)	-824.2
H_2(g)	0.0
Fe(s)	0.0
H_2O(l)	-285.830

By using these in Eq. (8.1), we find that

$$\Delta H = [3(-285.830) - (-824.2)]\mathrm{kJ/mol} = -33.29\mathrm{kJ/mol}. \qquad \{8.3)$$

Note that the calculated enthalpy change depends on how the reaction was written. For example, if we wrote

$$\frac{1}{2} Fe_2O_3(s) + \frac{3}{2} H_2(g) \overset{25\ ^oC,\ 1\ \mathrm{atm}}{\rightarrow} Fe(s) + \frac{3}{2} H_2O(l), \tag{8.4}$$

then $\Delta H = -16.65$ kJ/mol.

8.2. Measuring ΔH_f^0

There are a number of ways in which to measure the enthalpy of formation of a compound; here are two. The most obvious is to simply carry out the formation reaction from the constituent elements in their standard states in a constant pressure calorimeter (recall that $\Delta H = Q_p$).

For example, consider the combustion of graphite to form carbon dioxide

$$C(graphite) + O_2(g) \overset{25\ ^oC,\ 1\ \text{atm}}{\rightarrow} CO_2(g). \tag{8.5}$$

The heat released in this reaction is $-\Delta H_f^0(CO_2)$, since the standard enthalpy of formation of the reactants is zero. Note that the enthalpy change in this sort of reaction is also referred to as the heat of combustion.

For this method to work, two conditions must be met: 1) the reaction goes to completion and 2) only one product is formed. Thus, the reaction

$$C(graphite) + 2H_2(g) \overset{25\ ^oC,\ 1\ \text{atm}}{\rightarrow} CH_4(g) \tag{8.6}$$

is not suitable for this method since it doesn't readily go to completion and we get a complicated mixture of hydrocarbons.

In order to get around this, note that it is often possible to burn something to completion (and measure $\Delta H_{combustion}$, the heat released). Thus consider

$$CH_4(g) + 2O_2 \overset{25\ ^oC,\ 1\ \text{atm}}{\rightarrow} CO_2(g) + 2H_2O(l). \tag{8.7}$$

Equation (8.1) gives

$$\Delta H_{combustion} = \Delta H_f^0(CO_2(g)) + 2\Delta H_f^0(H_2O(l)) - \Delta H_f^0(CH_4(g)). \tag{8.8}$$

The standard enthalpies of formation of carbon dioxide and water can be measured using the first method; hence, once we measure the heat of combustion, the only unknown is the standard enthalpy of formation of methane (CH_4) and a little algebra gives:

$$\Delta H_f^0(CH_4(g)) = \Delta H_f^0(CO_2(g)) + 2\Delta H_f^0(H_2O(l)) - \Delta H_{combustion}.$$

$$= [-398.51 + 2(-285.83) - (-890.36)]\text{kJ/mol} = -74.81\text{kJ/mol} \tag{8.9}$$

In general, in order to measure the enthalpy of formation, all you need to to is find any reaction where all but one of the standard enthalpies of formation are known and where the reaction goes to completion. These sorts of manipulations are valid because the enthalpy is a state function, and are referred to as Hess's law. Also note that the same arguments could be made for the energy changes (under constant volume conditions).

8.3. Reactions at Different Temperatures: Kirchoff's Law

What happens if the temperature at which you perform the reaction (either at constant P or V) is different than that of your table of enthalpies of formation. Since the enthalpy is a state function, an alternate path can be found whereby the enthalpy change, calculated using the temperature of your table, can be used. Consider the constant pressure case depicted below

$$\begin{tikzcd}
\text{Reactants} \arrow[r] \arrow[d, "\text{I}"'] & \text{Products} & (T_1) \\
\text{Reactants} \arrow[r] & \text{Products} \arrow[u, "\text{II}"'] & (T_0)
\end{tikzcd}$$

The enthalpy change for the reaction at T_1 is equal to the enthalpy change at T_0 plus the enthalpy change for paths 1 and 2. However, on 1 or 2, only the constant pressure heating or cooling of the reactants or products is performed (i.e., no chemical reaction takes place). Since the constant pressure heat capacity, C_P was defined as

$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_{P,N}, \tag{8.10}$$

the incremental heat absorbed by the system on 1 or 2 is $C_P dT$. Integrating gives:

$$\Delta H_1 = \int_{T_1}^{T_0} C_P(reactants)dT = -\int_{T_0}^{T_1} C_P(reactants)dT \tag{8.11}$$

and

$$\Delta H_2 = \int_{T_0}^{T_1} C_P(products)dT. \tag{8.12}$$

Adding the contributions together gives

$$\Delta H(T_1) = \Delta H(T_0) + \int_{T_0}^{T_1} \left[C_P(products) - C_P(reactants) \right] dT. \tag{8.13}$$

This is known as Kirchoff's law. What changes must be made for the energy?

Consider our example of the reduction of Fe_2O_3. What is the enthalpy change at 358K? We will assume that the heat capacities are constant over the temperature range 298 - 358 K.

Constant Pressure Heat Capacities at 1 atm and 25 C

Compound	C_P (J/mol/K)
Fe_2O_3(s)	103.8
H_2(g)	28.8
Fe(s)	25.1
H_2O(l)	75.3

Note that elements in their standard states do *not* have zero heat capacities. Using the data in the table, and the result of our earlier calculation gives

$$\Delta H_{rxn}(358K) = -33.29 + \frac{[2(25.1) + 3(75.3) - 103.8 - 3(28.8)][358 - 298]}{1000}$$

$$= -28.1\text{kJ/mol.}$$

Note that no change in phase occurred when we cooled (heated) the reactants (products). What changes would have to be made if the reaction was carried out at 400 K?

8.4. Bond Energies

Consider the combustion reaction of ethanol:

$$C_2H_5OH(l) + 3O_2 \overset{25\ ^oC,\ 1\ \text{atm}}{\rightarrow} 3H_2O(l) + 2CO_2(g). \tag{8.14}$$

The standard enthalpies of formation for these compounds are:

Standard Enthalpies of Formation at 25C

Compound	ΔH_f^0 (kJ/mol)
$C_2H_5OH(l)$	-277.7
$H_2O(l)$	-285.830
$CO_2(g)$	-393.51

which gives $\Delta H_{combustion} = 3 \times (-285.830) + 2 \times (-393.51) - (-277.7) = -1389 kJ/mol$ for the reaction as written. This is quite exothermic. Where does the energy come from? If you've been told that it's related to breaking bonds, you've been misinformed; as our example clearly shows, it comes from forming bonds, specifically the strong bonds in CO_2 and H_2O.

We can make this idea more quantitative as by considering the typical energies in bonds. This is a useful, albeit very approximate, way to calculate enthalpy changes in chemical reactions. Consider the following reaction

$$CH_4 \rightarrow CH_3 + H; \tag{8.15}$$

i.e., one C-H bond is broken. Experimentally, ΔH for this reaction is 102 kcal/mol. Similarly, ΔH = 96 kcal/mol for

$$C_2H_6 \rightarrow C_2H_5 + H. \tag{8.16}$$

A survey of such reactions will show that the heat required to break a single C-H bond is in the range 96-102 kcal/mol. We can thus assign 98 kcal/mol as an average bond energy for the C-H bond. Similar tends are observed in the bond strength of other types of bonds, and the results are summarized in the following table

Average Bond Energies			
Bond	Energy (kcal/mol)	Bond	Energy (kcal/mol)
H-H	103	C-H	98
C-C	80	N-H	92
C=C	145	O-H	109
$C \equiv C$	198	Cl-H	102
N-N	37	Br-H	87
$N \equiv N$	225	I-H	71
O-O	34	C-Cl	78
O=O	117	C-N	66
Cl-Cl	57	$C \equiv N$	210
Br-Br	45	C-O	79
I-I	35	C=O	173

How can this be used? Consider the hydrogenation of ethlyene:

$$H_2C = CH_2 + H - H \rightarrow H_3C - CH_3. \tag{8.17}$$

At the molecular level, we break one H-H and one C=C bond, and form one C-C and two C-H bonds. The energy change is just the net energy left in the molecule in such a process. From the table, the bond breaking steps take 145+103=248 kcal/mol. The bond formation will give off 80+2(98)=276 kcal/mol. Hence the net energy change in the system is 248-276 = -28 kcal/mol. To get the enthalpy change, note that at constant pressure,

$$\Delta H = \Delta E + P\Delta V. \tag{8.18}$$

For this reaction, all reactants and products are gases. If we assume that the gases are ideal, we can compute ΔV; i.e.,

$$\Delta V = \frac{RT}{P} \Delta N. \tag{8.19}$$

Here $\Delta N = -1$ and thus

$$\Delta H = -28 - 1.9872 \times 10^{-3}\text{kcal/mol}/K \times 298K = -28.6 \text{ kcal/mol}.$$

(Note that here the difference between ΔH and ΔE is relatively small). The correct answer is -32.7 kcal/mol. Thus, while the bond energy method is not exact, it gives a reasonable estimate. The reason for the discrepancy is the assumption that the bond energy doesn't depend on what other bonds are present in the molecule--in general this is not true.

8.5. Some Manipulations Involving Thermodynamic Functions

8.5.1. The relationship between C_P and C_V

We know that

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} \quad \text{and that} \quad C_P = \left(\frac{\partial H}{\partial T}\right)_{N,P}. \tag{8.20}$$

How these two quantities are related is a good exercise in manipulating thermodynamic functions. Since $H \equiv E + PV$,

$$C_P = \left(\frac{\partial E}{\partial T}\right)_{N,P} + P\left(\frac{\partial V}{\partial T}\right)_{N,P}, \tag{8.21}$$

where the last derivative should be recognized as $V\alpha$, where α is the thermal expansion coefficient,

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{N,P}. \tag{8.22}$$

If we view the energy as a function of N,V,T,

$$\left(\frac{\partial E}{\partial T}\right)_{N,P} = \left(\frac{\partial E}{\partial T}\right)_{N,V} + \left(\frac{\partial E}{\partial V}\right)_{N,T}\left(\frac{\partial V}{\partial T}\right)_{N,P} = C_V + \alpha V\left(\frac{\partial E}{\partial V}\right)_{N,T}. \tag{8.23}$$

Hence,

$$C_P - C_V = \left[P + \left(\frac{\partial E}{\partial V}\right)_{N,T}\right]\alpha V = \frac{VT\alpha^2}{\kappa}, \tag{8.24}$$

where

$$\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} \tag{8.25}$$

is the isothermal compressibility, and where the last equality will be proven later. The compressibility must be positive (i.e., things get smaller when squeezed) and this implies that $C_P \geq C_V$. For an ideal gas, Joule showed that the internal energy per mol did not depend on the volume. In this case,

$$\bar{C}_P - \bar{C}_V = \alpha P\bar{V} = R. \tag{8.26}$$

8.5.2. The Joule-Thompson Experiment

Consider the following adiabatic (i.e, Q=0) process, whereby a gas is squeezed through a porous, rigid plug. Initially all the gas is in the left chamber, and is pushed by the piston through the porous plug, exerting a constant pressure, P_1. As this happens, the piston in the right chamber is withdrawn under constant pressure, P_2. Note that P_1 and P_2 are the opposing pressures discussed earlier, although the initial and final system pressures will be P_1 and P_2, respectively.

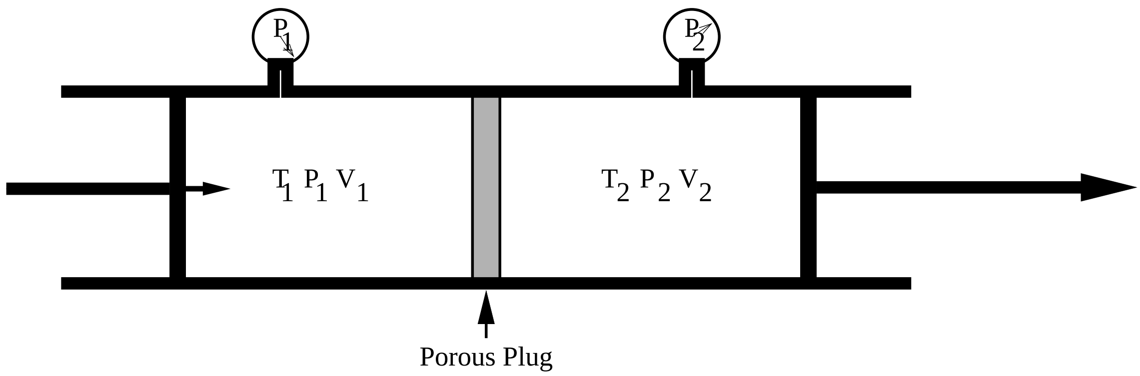


Fig. 8.1. The Joule-Thompson Experiment. Initially, the piston on the right is against the porous plug and the one on the left is withdrawn. As the experiment progresses, the piston on the left is moved in, keeping the pressure in the left chamber at P_1, and the one on the right is withdrawn, keeping the pressure in the right chamber at P_2.

Since, by assumption, Q=0,

$$\Delta E = E(P_2, V_2) - E(P_1, V_1) = W = P_1V_1 - P_2V_2. \tag{8.27}$$

By rearranging this expression we can show that

$$E(P_1, V_1) + P_1V_1 = E(P_2, V_2) + P_2V_2; \tag{8.28}$$

i.e., the enthalpy, H, is constant in the Joule-Thompson expansion.

In practice, large temperature changes can be obtained in this type of expansion (which can be used in designing a refrigerator or in liquefying gases). The key parameter is the so-called Joule-Thompson coefficient:

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_{H,N}. \tag{8.29}$$

In order to express μ_{JT} in terms of more readily measurable quantities, note that

$$\left(\frac{\partial y}{\partial x}\right)_f = -\frac{\left(\frac{\partial f}{\partial x}\right)_y}{\left(\frac{\partial f}{\partial y}\right)_x}, \tag{8.30}$$

which is sometimes known as the "cyclic rule" or "implicit function differentiation." It is proved by noting that

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy, \tag{8.31}$$

setting df=0, and by solving for the ratio dy/dx.

By using the cyclic rule in Eq. (8.29), we find that

$$\mu_{JT} = -\frac{\left(\frac{\partial H}{\partial P}\right)_{T,N}}{\left(\frac{\partial H}{\partial T}\right)_{P,N}} = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_{N,T} = -\frac{V}{C_P}\left\{1-\kappa\left[P+\left(\frac{\partial E}{\partial V}\right)_{N,T}\right]\right\}$$

$$= -\frac{V}{C_P}\left[1-\frac{\kappa}{\alpha V}(C_P - C_V)\right] = -\frac{V}{C_p}[1-\alpha T], \tag{8.32}$$

where the second to last equality follows when the definition of the enthalpy in terms of the energy is used and the manipulations used in calculating $C_P - C_V$ are repeated. κ is the isothermal compressibility. Note that the Joule-Thompson coefficient vanishes for an ideal-gas. This is not surprising given the kinetic theory of gases point of view; namely, we know that $\bar{E} = \frac{3}{2} RT$ and $\bar{H} = \bar{E} + PV/N = \frac{5}{2} RT$; hence, keeping H (and N) constant implies that T is constant.

It is interesting to consider physically why the non-ideal gas can change its temperature. According to problem 7.30 in Castellan, $\mu_{JT} = (2a/RT - b)/\bar{C}_p$ for the van der Waals gas. Thus, at low enough temperatures, it is the attractions and the van der Waals dimers that dominate μ_{JT} through the "a" coefficient. When we expand the gas, these dimers will dissociate and this requires energy; since the process is adiabatic, the only place where this energy can be obtained is from the kinetic energy of the gas, and hence, the temperature drops with a drop in pressure (i.e., $\mu_{JT} > 0$). At higher temperatures the steric interactions dominate; these are high-energy configurations, and reducing the pressure leads to these breaking up, releasing their energy to the system, thereby raising the temperature ($\mu_{JT} < 0$).

Note that the expression we just used for μ_{JT} is only valid for very dilute gases (with the usual caveats about the accuracy of the van der Waals equation). In general, there are higher order density corrections, and a more complete expression can be found by applying the cyclic rule to α, i.e.,

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} = -\frac{1}{V}\left(\frac{\partial P}{\partial T}\right)_{V,N} \div \left(\frac{\partial P}{\partial V}\right)_{T,N}. \tag{8.33}$$

By applying this to the van der Waals equation of state,

$$P = \frac{NRT}{V - Nb} - a\left(\frac{N}{V}\right)^2, \tag{8.34}$$

using the result in our last expression for μ_{JT}, and carrying out some simple algebra, we find that

$$\mu_{JT} = \frac{T_i(1 - b\rho)^2 - T}{\bar{C}_P[T - T_i b\rho(1 - b\rho)^2]}, \tag{8.35}$$

where $\rho \equiv N/V$ is the molar density and $T_i \equiv 2a/(Rb)$ is the inversion temperature (the temperature where the zero density Joule Thompson coefficient changes sign). Thus, we see that finite density systems have lower effective inversion temperatures; indeed by letting $T_i^{eff} \equiv 2a(1 - \rho b)^2/Rb < T_i$, it follows that

$$\mu_{JT} = \frac{1 - T/T_i^{eff}}{\bar{C}_P[T/T_i^{eff} - b\rho]}. \tag{8.36}$$

9. Ideal Gas Carnot Engines and Efficiency

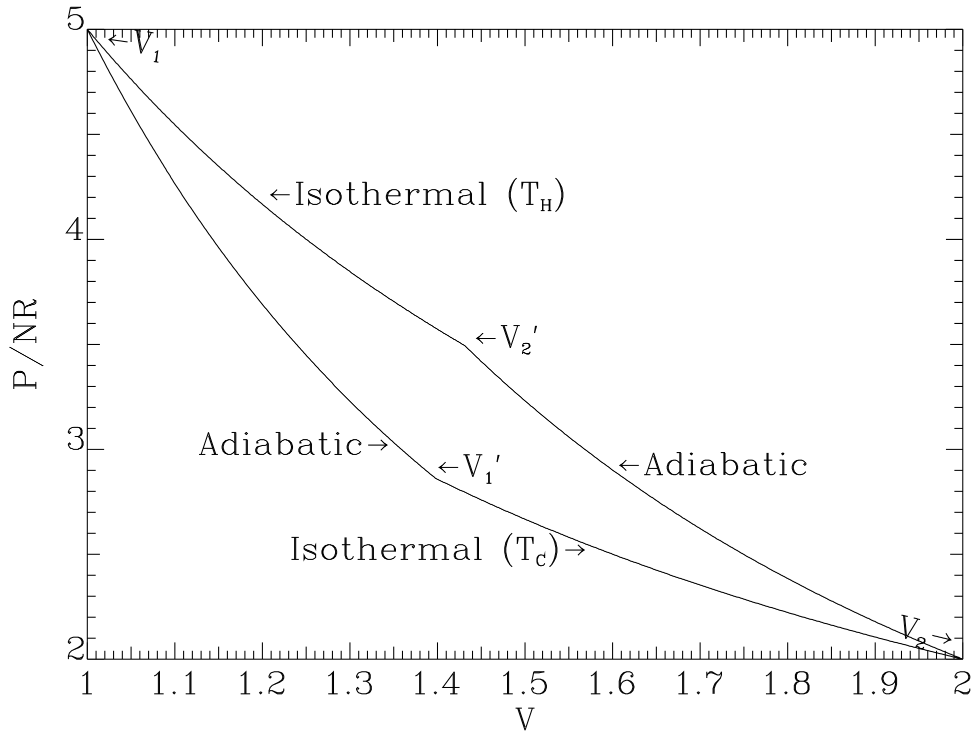


Fig. 9.1. The Carnot Cycle

The Carnot engine is a useful construction for relating the mathematical ($\Delta S \geq 0$ for a spontaneous process in an isolated system) and the physical statements of the Second Law of Thermodynamics (heat spontaneously flows from hot to cold, etc.). This section goes through the analysis of the amounts of work and heat produced in the isothermal and adiabatic parts of the Carnot cycle for an ideal gas.

9.1. Energy in an Ideal Gas: Joule's Experiment

In his study of the thermal properties of gases, Joule considered the isothermal expansion of dilute gases using the apparatus depicted below:

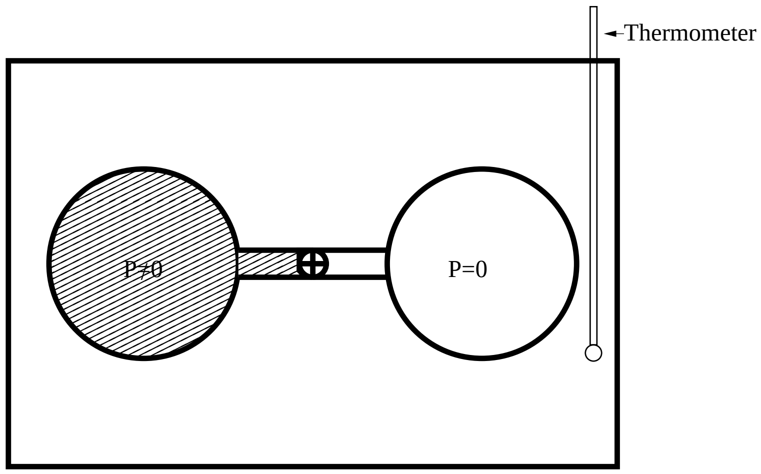


Fig. 9.2. Joule's Experiment

The bulb on the right was evacuated initially and heat was allowed to exchange with the heat bath, whose temperature was measured. For sufficiently dilute gases, Joule found that the temperature of the bath didn't change. This has some important consequences.

For this process, the system's (here the two bulbs) volume doesn't change, and hence, $W = 0$. Moreover, since the temperature of the bath remained constant, no heat was absorbed by the system, and thus $\Delta E = 0$. What does this say about the functional form of the energy of an ideal gas?

We know that we can write the energy of a one-component system as

$$E(N,V,T) = N\bar{E}(T, V/N),$$

where molar volume (the inverse of the molar density) was chosen instead of pressure as an independent variable (as can always be done if the equation of state is known). In Joule's experiment T and N were held fixed but the volume accessible by the gas, V, and hence N/V, changed. Nonetheless, E didn't change. Therefore, for an ideal gas,

$$E(N,V,T) = N\bar{E}(T);$$

i.e., the energy per mole of an ideal gas depends only on the temperature of the gas. Similarly, the heat capacity will only be a function of temperature (as it turns out, the heat capacity of an ideal gas is usually only weakly dependent on temperature). This shouldn't come as a total surprise, since our simple kinetic theory of gas model for the energy (translational energy) gave $E = \frac{3}{2} NRT$. Note that including other degrees of freedom for the molecular motion, e.g., vibration or rotation, will change the temperature dependence of $\bar{E}(T)$, but the lack of a volume dependence will remain.

9.2. Reversible, Adiabatic Expansion or Compression of an Ideal Gas

When an ideal gas is reversibly expanded (compressed) adiabatically, its temperature falls (rises). In order to relate the temperature and volume changes, we note that the energy of a ideal gas depends only on the temperature; hence,

$$dE = C_V dT = đQ + đW = đQ - NRT\,\frac{dV}{V}\,, \tag{9.1}$$

where C_V is the heat capacity at constant volume and where the last equality is obtained by using the ideal gas equation of state. For an adiabatic process, $đQ = 0$. After a little algebra, Eq. (9.1) can be rearranged to give:

$$\frac{C_V}{NR}\,\frac{dT}{T} = -\,\frac{dV}{V}\,.$$

If we assume that C_V is independent of temperature (this a good approximation for gases of simple molecules such as Ar, CO_2 etc.), this equality can be summed (or integrated) over the entire adiabatic expansion; that is,

$$\frac{C_V}{NR}\int_{T_{initial}}^{T_{final}} \frac{dT}{T} = \frac{C_V}{NR}\ln\left[\frac{T_{final}}{T_{initial}}\right] = -\int_{V_{initial}}^{V_{final}} \frac{dV}{V} = -\ln\left[\frac{V_{final}}{V_{initial}}\right], \tag{9.2}$$

where the integrals have been evaluated and "ln" is the natural logarithm function. Finally, both sides of Eq. (9.2) are exponentiated, and we find that

$$\frac{V_{initial}}{V_{final}} = \left(\frac{T_{final}}{T_{initial}}\right)^{C_V/NR} \quad \text{or} \quad \frac{P_{final}}{P_{initial}} = \left(\frac{T_{final}}{T_{initial}}\right)^{C_P/NR}, \tag{9.3}$$

where the second expression is obtained by noting that for ideal gases, $PV = NRT$ (even for an adiabatic change) and that $C_P = C_V + NR$. This shows how volume and temperature changes are related along an adiabatic path. (Again, no violation of Charles' or Boyle's laws is implied) Notice, if $V_{initial} < V_{final}$, then the gas is cooler after the expansion. This is to be expected since the expansion removes energy from the system, energy which is not replaced by the addition of heat from a heat reservoir.

Finally, for an adiabatic change in an ideal gas,

$$\Delta E = W = +\Delta U_{mechanical} = \int_{T_{initial}}^{T_{final}} C_V(T)dT \approx C_V \Delta T,$$

whether or not the path is reversible!

9.3. Reversible, Isothermal Expansion or Compression of an Ideal Gas

Since the energy of an ideal gas depends only on the temperature T, it remains constant during any isothermal process (i.e., dE = 0). From the first law, this implies that

$$đQ = -đW = PdV = NRT\,\frac{dV}{V}\,. \tag{9.4}$$

If the dQ's given by Eq. (9.4) are summed over the entire expansion (i.e., between the initial volume, $V_{initial}$ and the final volume, V_{final}) we find that

$$-W = Q_{isothermal} = NRT\int_{V_{initial}}^{V_{final}} \frac{dV}{V} = NRT\ln\left[\frac{V_{final}}{V_{initial}}\right], \tag{9.5}$$

9.4. Entropy Changes in the Ideal Gas Carnot Cycle

Next we use Eq. (9.5) for the isothermal portions of the Carnot cycle (see Fig. 1, part 1 and 3); it is easy to show that

$$\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = NR\ln\left[\frac{V_2' V_1'}{V_1 V_2}\right]. \tag{9.6}$$

However, if we use Eq. (9.3) on part 2 of the cycle, it follows that

$$\frac{V_2'}{V_2} = \left[\frac{T_C}{T_H}\right]^{C_V/NR}.$$

Similarly, for the adiabatic compression,

$$\frac{V_1'}{V_1} = \left[\frac{T_H}{T_C}\right]^{C_V/NR}.$$

Thus, if we use these two expressions in Eq. (9.6) the argument of the logarithm becomes equal to 1, and

$$\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0. \tag{9.7}$$

This is an explicit demonstration of the Second Law of Thermodynamics (i.e., that the entropy is a state function).

Note that the efficiency, (denoted by the Greek letter eta, η), of the Carnot cycle (i.e., how much work is produced per unit heat absorbed) is easily obtained using Eq. (9.7):

$$\eta \equiv \frac{-W}{Q_H} = \frac{Q_H + Q_C}{Q_H} = 1 - \frac{T_C}{T_H}\,, \tag{9.8}$$

where the second equality follows form the first law and where the last equality follows from Eq. (9.7). As is shown on the following pages, this efficiency formula must hold no matter what the working fluid in the Carnot engine, and hence, Eq. (9.7) must hold for materials other than ideal gases.

Note that running the Carnot engine backwards creates a refrigerator or heat pump; work is is added to the system and pumps heat from hot to cold (simply reverse the signs on the Q's and W's in our preceding calculation to see this). For our purposes we won't distinguish between the efficiency of a Carnot engine or refrigerator, both will be defined as if the refrigerator was run backwards as an engine, thereby giving Eq. (9.8). On the other hand it is interesting to consider the efficiency of a refrigerator, defined in terms that would be meaningful to a consumer (say browsing refrigerators in Sears). A reasonable definition is:

$$\text{Efficiency}_{\text{Refrigerator}} = \frac{Q_C}{W}\,; \tag{9.9}$$

i.e., the amount of heat pumped out of the cold reservoir, i.e., the ice box, into the carnot cycle refrigerator per unit work done on the system. By repeating the steps that led to Eq. (9.8) it is easy to see that

$$\text{Efficiency}_{\text{Refrigerator}} = -\frac{Q_C}{Q_C + Q_H} = \frac{T_C}{T_H - T_C} = \frac{1}{\eta_{\text{Engine}}} - 1. \tag{9.10}$$

Note that the refrigerator efficiency becomes infinite as $T_H \to T_C$ and is ≤ 1 for $T_H \geq 2T_C$. For example, taking $T_C = 274.75K$ (1.6 C) and $T_H = 293.15K$ (20 C), gives $\eta_{\text{Refrigerator}} = 14.9$.

Finally, for a heat pump,

$$\text{Efficiency}_{\text{Heat Pump}} = -\frac{Q_H}{W} = \frac{1}{\eta_{\text{Engine}}} = \frac{Q_H}{Q_H + Q_C} = \frac{T_H}{T_H - T_C} > 1, \tag{9.11}$$

which also diverges as $T_H \to T_C$; this is the reason why heat pumps are very efficient ways to heat homes in the winter. For example, if it's 20C inside and 0C outside, the Carnot heat pump efficiency is 15! That is, you get 15J of heat for every joule of energy used to run the pump. (In reality, you can get close to this theoretical limit only for certain temperature ranges--when the temperature is very low, the operation of the heat pump becomes inefficient, i.e., irreversible).

10. Ideal Gas Carnot Engines and Efficiency

The second law of thermodynamics gives information concerning the direction of spontaneous change. If the second law says that a certain process is impossible, you will not be able to get the process to go. On the other hand, note that if the second law says that a process is possible, you still have to worry about kinetics--you have to find a way in which to carry out the process in a reasonable amount of time.

There are a number of equivalent physical statements of the second law of thermodynamics. According to Kubo (Thermodynamics, North Holland Publishing Co., 1976) they are:

1. **Clausius principle**: A process which involves no change other than the transfer of heat from a hotter body to a cooler body is irreversible; or, it is impossible for heat to transfer spontaneously from a colder to a hotter body without causing other changes.

2. **Thompson's (or Kelvin's) principle**: A process in which work is transformed into heat without any other changes is irreversible; or, it is impossible to convert all the heat taken from a body of uniform temperature into work without causing other changes.

3. **Impossibility of perpetual motion of the second kind**: (due to Max Planck) It is impossible to devise an engine operating in a *cycle* which does work by taking heat from a single heat reservoir without producing any other change.

4. **Caratheodory's principle**: For a given thermal equilibrium state of a thermally uniform system, there exists another state which is arbitrarily close to it, but which can never be reached from it by an adiabatic change.

   Any of these physical statements can be used to prove the others, and to finally prove the mathematical statement of the second law of thermodynamics:

5. Any spontaneous process satisfies the Clausius inequality:

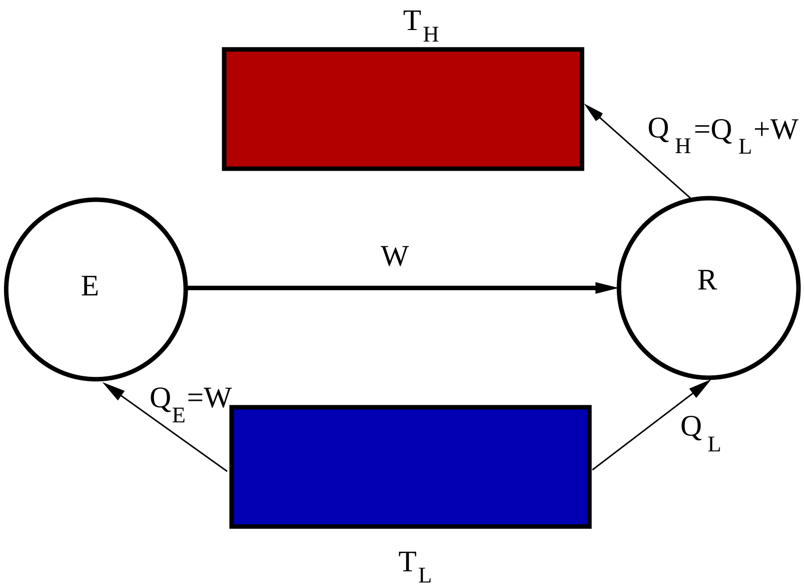
$$\oint \frac{đQ}{T} \leq 0$$

which implies that there exists a state function, the entropy (denoted by the letter S)

$$\Delta S \geq \int \frac{đQ}{T}$$

where, in either expression, the equality holds when the process is reversible.

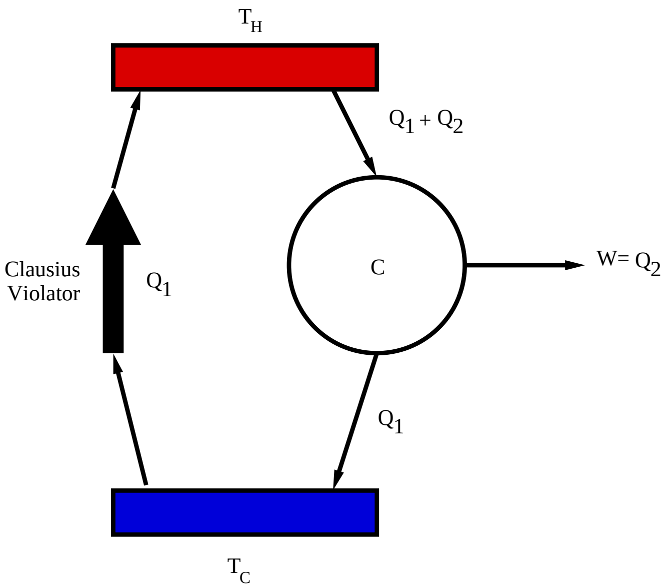
Before showing how 1.-4. imply 5., let's first consider how the different physical statements imply one another. For example, how does one show that Clausius' principle implies Thompson's? Suppose it didn't; i.e., Clausius's principle is correct, but Thompson's is not. This means that you can build an engine which produces work, and which is connected to a single heat reservoir. If so, consider the following device:



where, E is the Thompson violator, and R is a Carnot refrigerator.

If we adjust the sizes of E and R such that all the work is used to run the Carnot refrigerator, and view the combined E-R apparatus as the system, we have succeeded in creating a device, which spontaneously pumps heat from cold to hot without any work input from the surroundings. This violates Clausius' principle and thus we have proved Thompson's principle by contradiction.

Similarly, we can use Thompson's principle to prove Clausius'. Again, the proof is by contradiction. If Clausius's principle is untrue, then you can find a device which spontaneously (i.e., without any work input) transfers heat from a colder body to a hotter one. Consider the following apparatus:



where C is a Carnot engine and where the sizes of the Carnot engine and our Clausius violator are adjusted such that the heats transferred are as indicated.

What is the net result after one cycle? Work has been produced in the surroundings, but there is no net change in the heat content in the cooler reservoir. Hence, it is as if the system were operating in contact with a single reservoir and producing work in the surroundings, in contradiction to Thompson's principle.

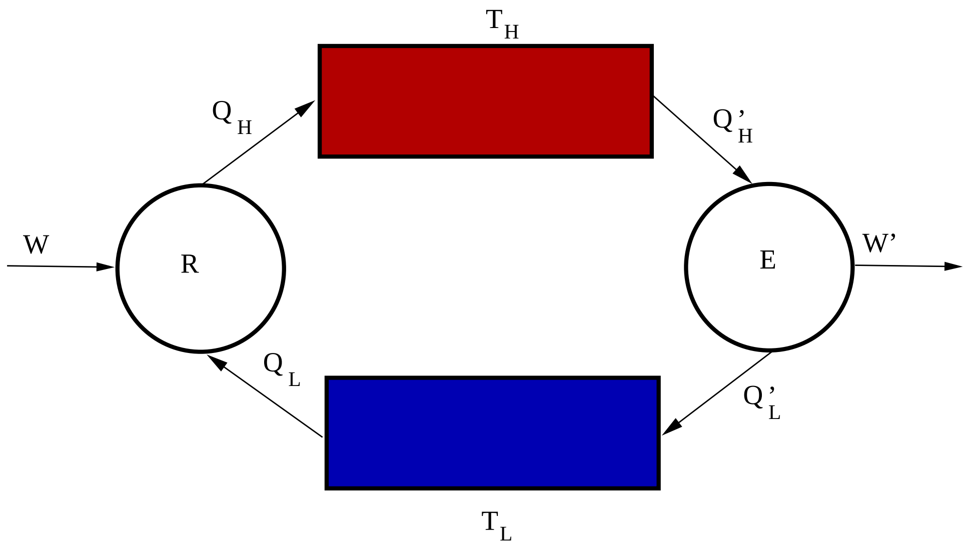
These kind of arguments can be used to prove the equivalence of the other physical formulations of the second law.

10.1. Efficiency of Real Carnot Engines

Why is the Efficiency of a Carnot Engine Independent of the Kind of Working Material?

Here are two proofs that the efficiency of any reversible Carnot engine is the same and depends only on the temperatures of the heat baths.

10.1.1. Method I using Thompson's Principle



where

W'	= the work produced by the engine,
Q_H'	= the heat absorbed by the engine from the hot reservoir,
Q_L'	= the heat given off by the engine to the cooler reservoir,
W	= the work used to run the Carnot refrigerator,
Q_H	= the heat given off by the refrigerator to the hot reservoir,
Q_L	= the heat absorbed by the refrigerator from the cooler reservoir.

The sizes of the engine and refrigerator are adjusted such that no net heat is taken from the cool reservoir in one cycle (i.e., $Q_L = Q_L{}'$). According to Thompson's principle, no net positive work can be realized in the surroundings from any device which takes heat from a single heat source. Thus,

$$W' - W \leq 0. \tag{10.1.1.1}$$

However, from the First Law, the net work produced must equal the net heat absorbed by the system; i.e.,

$$W' - W = Q_H{}' - Q_H. \tag{10.1.1.2}$$

If we denote the "engine efficiencies" of the refrigerator and engine as η and η', respectively, Eq. (10.1.1.2) can be rewritten as:

$$(1-\eta') = (1-\eta)\,\frac{Q_H}{Q_H{}'} \geq (1-\eta). \tag{10.1.1.3}$$

The last inequality follows from Eqs. (10.1.1.1) and (10.1.1.2), i.e., $Q_H \geq Q_{H'}$ and hence, $Q_H/Q_H{}' \geq 1$. By rearranging Eq. (10.1.1.3) we see that

$$\eta \geq \eta'. \tag{10.1.1.4}$$

That is, the engine efficiency of the refrigerator is greater than that of the engine, no matter what.

Note that Eq. (10.1.1.4) is valid even if one or both of the engines is not reversible. If both engines are reversible, then the roles of engine and refrigerator can be interchanged and we conclude that

$$\eta' \geq \eta. \tag{10.1.1.5}$$

In light of Eq. (10.1.1.4) this is possible only if $\eta = \eta'$. Note that for this case, the net work produced by the device is zero!.

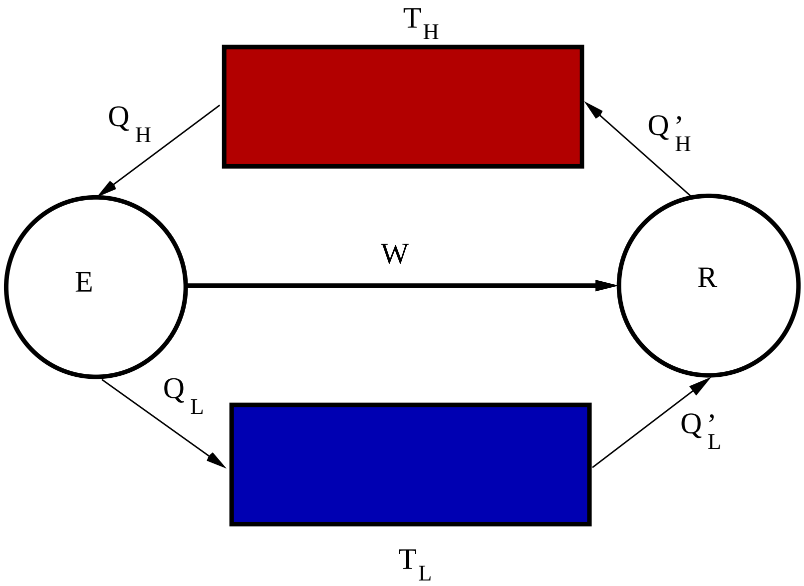
Thus we have shown that the engine efficiency of all reversible Carnot cycle engines are the same; since this includes the ideal gas Carnot engine we analyzed earlier it follows that

$$\eta_{REV} = 1 - \frac{T_L}{T_H}\,. \tag{10.1.1.6}$$

Finally, if the engine is irreversible, an upper bound to its efficiency can be obtained by using a reversible refrigerator. In this case, Eq. (10.1.1.4) implies that

$$\eta_{IR} \leq \eta_{REV} = 1 - \frac{T_L}{T_H}\,. \tag{10.1.1.7}$$

10.1.2. Method II using Clausius' Principle



where

W	= the work produced by the engine
Q_H	= the heat absorbed by the engine from the hot heat bath
Q_L	= the heat released by the engine to the cool heat bath
Q'_H	= the heat released by the refrigerator to the hot heat bath
Q'_L	= the heat absorbed by the refrigerator from the cool heat bath

We will assume that the Carnot engine is more efficient than the Carnot refrigerator and that the size of the engine is adjusted so that the work output of the former equals that needed to run the latter; i.e.,

$$\eta_E = \frac{W}{Q_H} > \eta_R = \frac{W}{Q'_H} \,. \tag{10.1.2.1}$$

By assumption therefore,

$$Q_H < Q'_H. \tag{10.1.2.2}$$

Since the engine and the refrigerator run in a cycle, the first law tells us that ($\Delta E = 0$):

$$W = Q_H - Q_L = Q'_H - Q'_L, \tag{10.1.2.3}$$

which when combined with (10.1.2.2) shows that

$$Q_L - Q_L{}' = Q_H - Q'_H < 0. \tag{10.1.2.4}$$

What does this mean? The quantity $Q_H - Q'_H$ is the net heat taken **OUT** of the hotter heat source. However, cf. Eq. (10.1.2.4), we have just shown that it is negative; i.e., a net amount of heat (>0) has been transferred **INTO** the hotter heat source from the cooler one. No net work has been done by the surroundings (i.e., by us), and thus our initial assumption violates Clausius' statement of the second law of thermodynamics. Hence, we must conclude that $\eta_E \leq \eta_R$. This reverses the inequality in Eq. (10.1.2.4); i.e., now the net heat taken **OUT** of the hotter body and going **INTO** the colder one is positive, and does not violate Clausius' statement of the second law.

If both the engine and refrigerator are reversible, then they can both be run in reverse; hence the engine now acts as a refrigerator and the refrigerator as an engine. All the signs on work and heat flip and we conclude that $\eta_R \leq \eta_E$ (where the R and E refer to the original devices). The only way out of this contradiction is for the efficiencies of all reversible Carnot cycles to be equal no matter what the nature of the material in the engine or refrigerator.

10.2. The Clausius Inequality and the Second Law

Here is a proof of the Clausius inequality relating the word and mathematical statements of the Second Law. Consider the device shown in the following figure:

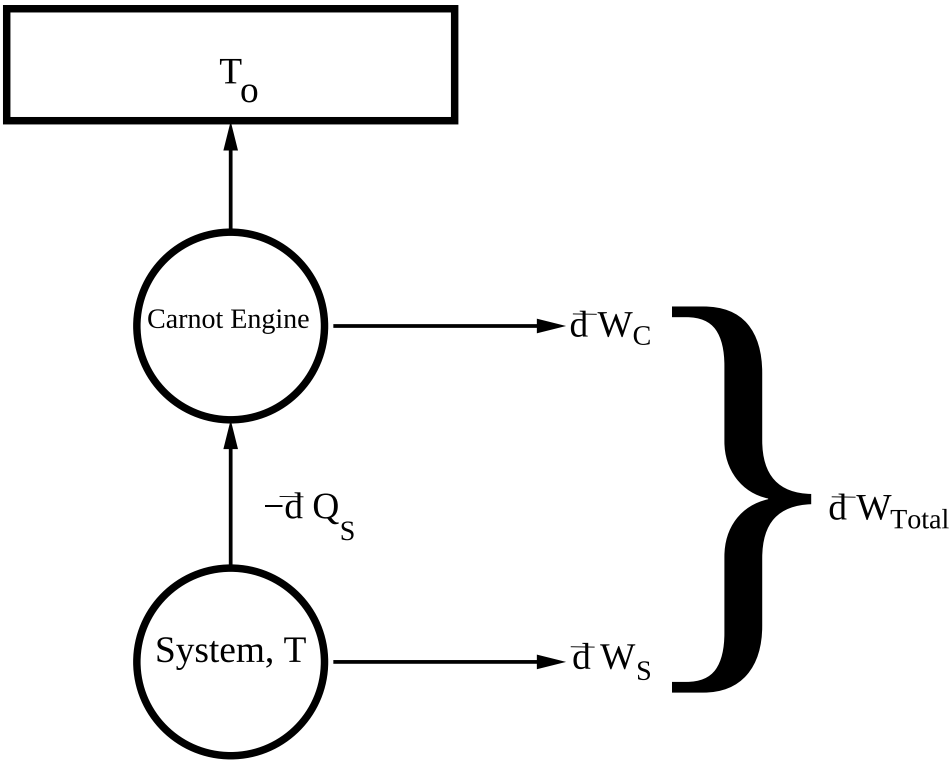


Fig. 10.2.1. A reversible Carnot engine takes heat $-đQ_s$ from a part of the system at temperature T, produces work, $đW_c$, in the surroundings, and gives the remaining heat to a reservoir at temperature T_0. While this happens, the system absorbs heat $đQ_s$ and produces work $đW_s$.

From our definition of efficiency and the fact that the efficiencies of all reversible Carnot engine are the same (cf. previous section), we have:

$$đW_c = -\eta_c đQ_s = \left(\frac{T_o}{T} - 1\right) đQ_s. \tag{10.2.1}$$

From Kelvin/Thompson's principle and Eq. (10.2.1), it follows that

$$W_{Total} = \oint đW_s + đW_c = \oint đW_s + \left(\frac{T_o}{T} - 1\right) đQ_s \le 0. \tag{10.2.2}$$

This inequality must hold if the process is to proceed as written. Now we integrate Eq. (10.2.2) around one cycle of the system (reversible or not) and use the fact that the system's energy is conserved; i.e.,

$$\oint đW_s = \oint đQ_s.$$

After a little algebra, this gives:

$$\oint \frac{đQ_s}{T} \le 0, \tag{10.2.3}$$

where the constant, positive multiplicative factor, T_0, has been dropped. This is the Clausius inequality.

Equation (10.2.3) holds for **any** spontaneous process which can occur in the system; although, all irreversible processes will require a net work input in order to run in the configuration depicted above. The inequality in Thompson's principle, cf. the last chapter, becomes an equality only for reversible processes (no matter what the path) and thus Eq. (10.2.3) becomes:

$$0 = \oint \frac{đQ_{rev}}{T} \equiv \oint dS, \tag{10.2.4}$$

where the entropy is defined along any reversible path (Eq. (10.2.4) is a proof that it is a state function) through

$$dS \equiv \frac{đQ_{rev}}{T}. \tag{10.2.5}$$

Proof that $dS \ge \frac{đQ}{T}$

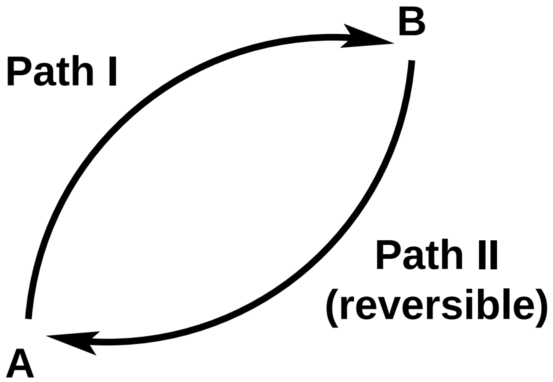


Fig. 10.2.2.

Consider some process, cf. Fig. 10.2.2, whereby a system changes from state A to B along path I; the process may be reversible or irreversible. After the $A \rightarrow B$, path I, process is finished, the system is restored to its initial state (A) along a reversible path II. If we apply the Clausius inequality to this cycle, we have

$$\int_{A,\ path\ I}^{B} \frac{đ\, Q_I}{T} + \int_{B,\ path\ II}^{A} \frac{đ\, Q_{rev}}{T} \leq 0. \tag{10.2.1}$$

Since path II is reversible, the process can be carried out in reverse (*This is not necessarily true for path I*) and thus:

$$\int_{B,\ path\ II}^{A} \frac{đ\, Q_{rev}}{T} = -\int_{A,\ path\ II}^{B} \frac{đ\, Q_{rev}}{T} = -\Delta S_{A\to B}. \tag{10.2.2}$$

By using Eq. (10.2.2) in Eq. (10.2.1) we conclude that

$$\Delta S_{A\to B} \geq \int_A^B \frac{đ\, Q_I}{T},$$

or for infinitesimal changes

$$dS \geq \frac{đ\, Q}{T}.$$

Note that the equality holds only for reversible processes.

10.3. Entropy Calculations

We have shown that the entropy, defined through its differential as

$$dS = \frac{đ\, Q_{Reversible}}{T}, \tag{10.3.1}$$

is an extensive (because Q is) state function with units of energy/K; hence,

$$\oint \frac{đ\, Q_{Reversible}}{T} = 0. \tag{10.3.2}$$

Since entropy is a state function (according to Eq. (10.3.2)), we can use *any* reversible path to calculate it, and are guaranteed to get the same answer (something you demonstrated in homework).

How do you calculate entropy changes? Clearly from Eq. (10.3.1)

$$\Delta S_{A\to B} = \int_A^B \frac{đ\, Q_{Reversible}}{T}, \tag{10.3.3}$$

but how do you use this? The first criterion is to find a reversible path connecting your initial and final states. In some cases, this is almost all you have to do. For example, suppose the system is at constant volume. We know that $dQ_V = C_V dT$, which when used in Eq. (10.3.3) shows that

$$\Delta S_{T_i\to T_f} = S(T_f, V, N) - S(T_i, V, N) = \int_{T_i}^{T_f} \frac{C_V(T, V, N)}{T}\, dT \approx C_V \ln\left(\frac{T_f}{T_i}\right), \tag{10.3.4a}$$

where the last approximation follows by assuming that C_V is independent of temperature (at least approximately).

Similarly, if instead the pressure is held constant, we have $dQ_P = C_P dT$ and Eq. (10.3.3) becomes

$$\Delta S_{T_i \to T_f} = S(T_f, P, N) - S(T_i, P, N) = \int_{T_i}^{T_f} \frac{C_P(T, P, N)}{T}\, dT \approx C_P \ln\left(\frac{T_f}{T_i}\right), \quad (10.3.4b)$$

where we have again treated C_P as approximately constant to get the last relation. In general, note that $\Delta S_{T_i \to T_f}$ are *not* the same in constant volume and pressure processes.

What happens if there is a phase change somewhere between T_i and T_f, e.g., at T_0? At the phase transition, heat (e.g., the latent heat of fusion, sublimation, or vaporization) is added to the system, with no resulting change in temperature, until all the material is converted from one phase to another. At constant pressure, the contribution to the entropy is just $\Delta H_{transition}/T_0$ (what is it for constant volume?) and we can write

$$\Delta S_{T_i \to T_f} = \int_{T_i}^{T_0} \frac{C_{P,i}(T, P, N)}{T}\, dT + \frac{\Delta H_{transition}}{T_0} + \int_{T_0}^{T_f} \frac{C_{P,f}(T, P, N)}{T}\, dT, \quad (10.3.5)$$

where $C_{P,i/f}$ is the heat capacity in the initial/final phase. For example, if we were to warm one mole of ice from -10C (263K) to 10C (283K) at 1 atm, Eq. (10.3.5) gives (treating the heat capacities as constants):

$$\Delta S = C_P(ice) \ln\left(\frac{273}{263}\right) + \frac{\Delta H_{fus}}{273} + C_P(water) \ln\left(\frac{283}{273}\right), \quad (10.3.6)$$

where ΔH_{fus} is the molar heat of fusion of water. Similarly, warming 1 mole of water from 90C (363K) to 110C (383K) gives

$$\Delta S = C_P(water) \ln\left(\frac{373}{363}\right) + \frac{\Delta H_{vap}}{373} + C_P(steam) \ln\left(\frac{383}{373}\right), \quad (10.3.7)$$

where ΔH_{vap} is the latent heat of vaporization for water. Note that there is an empirical relation, known as Trouton's rule, which asserts that for many liquids, $\Delta S_{vap} = \Delta H_{vap}/T_b \approx 90 J/K/mol$. There are, however, many examples where the rule fails (e.g., water, alcohols, amines). (As a review exercise, calculate the enthalpy changes for the two examples given in Eqs. (10.3.6) and (10.3.7)).

Matters become somewhat more complicated if neither pressure or volume is held constant, but we will soon have the tools needed to handle the general case.

11. The Third Law of Thermodynamics

The preceding section has shown how to compute entropy changes in much the same way as we did for enthalpy and energy changes. What happens in a chemical reaction? Since S is a state function, we can imagine the reaction proceeding by way of the constituent elements in their standard states of aggregation, and exactly as was done for the enthalpy,

$$\Delta S = \Delta S_f(products) - \Delta S_f(reactants). \tag{11.1}$$

How should we define the standard state? You might think that it should be defined exactly as it was for the enthalpy; i.e., pure elements at 1 atm in their standard states of aggregation are arbitrarily assigned zero entropy of formation. While there is nothing wrong with this, it turns out that experiments performed in the early 20'th century suggest another choice.

In 1902, T.W. Richards found, for a wide class of reactions, that the entropy of reaction approached zero as the temperature approached absolute zero. In 1906, using Richards' data, Nernst argued that this meant that all materials have the same entropy at absolute zero (which can arbitrarily assigned to be zero). This was summarized by Planck in 1912 in what is now known as the Third Law of Thermodynamics:

The entropy of all perfect crystalline solids at absolute zero is zero.

There is a good microscopic reason for this, albeit one that is beyond the level of this course. As many of you may have seen in your general chemistry course, there is a relationship between entropy and randomness; specifically, cf. the section on entropy of mixing in ideal systems, $S = k_B \ln \Omega$, where Ω is the number of ways of realizing the system. If there is only one way to realize the system, the entropy is zero and this turns out to be the case for perfect crystals at absolute zero.

The third law leads to the introduction of an absolute entropy scale, where all entropies (of perfect crystalline states) are zero at absolute zero; hence, at any finite temperature

$$S(T, P, N) = \int_0^T \frac{dQ_P}{T} = \int_0^T \frac{C_P}{T}\, dT, \tag{11.2}$$

where a similar expression holds in terms of C_V for constant volume processes. The last expression must be modified slightly if phase transitions occur between 0K and T (as above). In practice, this means that entropies of formation of the pure elements at 298.15 and 1 atm are *NOT* zero!

You might think that the preceding discussion is just an argument about some convention. In part you would be correct; either convention would give identical answers in ΔS calculations. However, the Third Law does have at least one important physical consequence; namely, that heat capacities must vanish as absolute zero is approached. If this weren't the case then the last integral in Eq. (11.9) would diverge logarithmically, and the entropy would be infinite, not zero! This is indeed the case experimentally, although sometimes extraordinarily low temperatures must be attained to see the heat capacities vanish. One troubling result is our prediction from the kinetic theory of gases, which gave $\bar{C}_V = \frac{3}{2} R$ and $\bar{C}_P = \frac{5}{2} R$, *independent of temperature* and clearly nonzero. Again, the detailed answer lies beyond this course, but in short, the third law is intimately bound to quantum mechanics and energy quantization, something our simple kinetic theory model had completely ignored.

12. The Chemical Potential

Up to now, we have not seriously considered the consequences of changing the composition of a thermodynamic system. In practice, this can happen in two ways: 1) by externally adding or removing material or 2) by changing the composition through chemical reaction. Nonetheless, as far as state functions are concerned, the same results must be considered.

There is an energy change associated with changing the composition of the system. For example, you may add compounds with different types of bonds and this will change the energy available to carry out other processes (e.g., via combustion).

In order to account for the energy change associated with adding material to the system we introduce a new kind of work done on the system:

$$đW_i \equiv \mu_{i,op} dN_i, \tag{12.1}$$

where dN_i is the change in the amount of the i'th component (i.e., mass, number of moles, etc.) and where $\mu_{i,op}$ is called the opposing chemical potential (and is analogous to the opposing pressure). For reversible processes, the opposing chemical potential equals the chemical potential, μ_i, of component i in the system. In general, the chemical potential for component i in a system is intensive and is a function of T,P, composition and phase. Moreover, like the equation of state, it must be measured or calculated from a microscopic theory, and we will consider some specific examples later.

The energy change of the system can now be written as:

$$dE = đQ - P_{op}dV + \sum_i \mu_{i,op} dN_i \tag{12.2}$$

or for reversible paths as

$$dE = TdS - PdV + \sum_i \mu_i dN_i. \tag{12.3}$$

Henceforth, we will restrict ourselves to processes where the addition of matter is reversible and thus drop the subscript "op" on μ.

Equation (12.2) has an interesting consequence. If we view the energy of a system as a function of S, V, and the N_i (all of which are extensive), then the steps that lead to our application of Euler's theorem to extensive quantities imply that

$$E(S,V,N_i) = \left(\frac{\partial E}{\partial S}\right)_{V,N_i} S + \left(\frac{\partial E}{\partial V}\right)_{S,N_i} V + \sum_i \left(\frac{\partial E}{\partial N_i}\right)_{S,V,N_{j\neq i}} N_i.$$

(Simply replace some of the N_i's by S and V, both of which are also extensive). The partial derivatives immediately follow from Eq. (12.4), and we find that

$$E = TS - PV + \sum_i \mu_i N_i. \tag{12.4}$$

We also obtain the Gibbs-Duhem equation

$$0 = SdT - VdP + \sum_i N_i d\mu_i. \tag{12.5}$$

By using Eq. (12.4) and $H \equiv E + PV$, it follows that

$$H = TS + \sum_i \mu_i N_i. \tag{12.6}$$

As we will see, the chemical potentials play a key role in any quantitative analysis of chemical equilibria.

13. State Functions, Exact Differentials, and Maxwell Relations

Consider the differential form:

$$df \equiv M(x, y)dx + N(x, y)dy. \tag{13.1}$$

If can we define a **single-valued,** differentiable function f(x,y) which satisfies Eq. (13.1), then $M(x, y)dx + N(x, y)dy$ is said to be an exact differential. Of course, we can always define f(x,y) by integrating the right hand side of Eq. (13.1) along some path; however, we require that the function be single-valued (i.e., that it be a state function); hence, different paths must give the same answer.

THEOREM:

If M and N have continuous first partial derivatives at all points of some open rectangle, the differential form, (13.1), is exact at each point of the rectangle if and only if the condition

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \tag{13.2}$$

is satisfied throughout the rectangle. When this holds, the function f(x,y) is given by the line integral

$$f(x, y) = \int_C M(s, t)ds + N(s, t)dt \tag{13.3}$$

along a path from (a,b) to (x,y), e.g., as shown in Fig. 13.1.

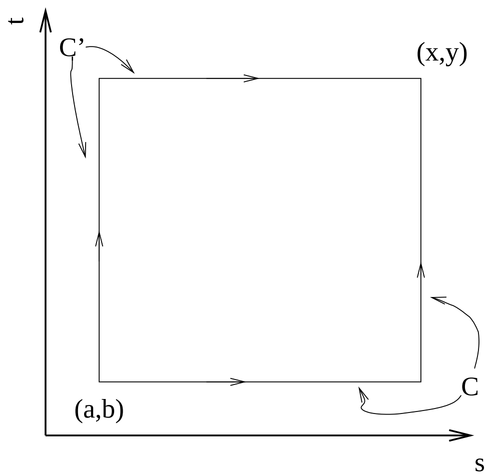


Fig. 13.1. Two paths, C and C', connecting state (a, b) and (x, y). For a state function, you have to get the same answer, no matter which path is used.

The proof is given in the Appendix (*you are not responsible for the proof, but you must know how to use the result*).

13.1. Applications to Thermodynamics: Maxwell Relations

We have been able to combine the first and second laws of thermodynamics to write

$$dE = TdS - PdV, \tag{13.4}$$

where N is held constant for this discussion. Since E is a state function, Eq. (13.2) must hold, and thus Eq. (13.4) gives

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V. \tag{13.5}$$

This is called a Maxwell relation and is a powerful tool for relating different quantities thermodynamics.

Another Maxwell relation can be obtained from the enthalpy for which

$$dH = TdS + VdP. \tag{13.6}$$

Hence, Eq. (13.2) gives

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{13.7}$$

Clearly every state function will generate one or more Maxwell relations. The trick is to know which ones to use in any given application.

13.2. Maxwell Relations: A Complicated Example

Suppose we want to express the change in the entropy as a function of T and P (i.e., choose a thermodynamic point of view). To begin, note that

$$dS = \left(\frac{\partial S}{\partial T}\right)_{P,N} dT + \left(\frac{\partial S}{\partial P}\right)_{T,N} dP + \bar{S}dN,$$

where $\bar{S}$ is the partial molar entropy (remember that entropy is extensive and Euler's theorem must hold). The term in dT is easy to reexpress. When the pressure is constant, the change in the entropy is

$$dS = \frac{đQ_P}{T} = \frac{C_P}{T}dT$$

and thus

$$dS = \frac{C_P}{T}dT + \left(\frac{\partial S}{\partial P}\right)_{T,N} dP + \bar{S}dN.$$

A new entropy derivative still remains to be reexpressed in terms of something more conventional. To do so we will use a Maxwell relation. We know that

$$\frac{\partial^2 H}{\partial T \partial P} = \frac{\partial^2 H}{\partial P \partial T}\,; \tag{13.8}$$

however, from Eq. (13.6)

$$LHS = \frac{\partial}{\partial T}\left[T\left(\frac{\partial S}{\partial P}\right)_{T,N} + V \right] = \left(\frac{\partial S}{\partial P}\right)_{T,N} + T\,\frac{\partial^2 S}{\partial T \partial P} + V\alpha,$$

where recall that $V\alpha = (\partial V/\partial T)_{P,N}$. Similarly,

$$RHS = \frac{\partial}{\partial P}\left[T\left(\frac{\partial S}{\partial T}\right)_{N,P} \right] = T\,\frac{\partial^2 S}{\partial P \partial T}\,.$$

Since the entropy is a state function, its mixed second derivatives must be equal; hence, equating the LHS and RHS of Eq. (13.8) and carrying out some algebra gives:

$$\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N} = -V\alpha. \tag{13.9}$$

Thus, we have succeeded in expressing the change in the entropy in terms of readily measurable quantities; namely

$$dS = \frac{C_P}{T}\,dT - V\alpha dP + \bar{S}dN. \tag{13.10}$$

(Actually, there is a much simpler route to Eq. (13.9) using the Maxwell relation for the Gibb's Free energy, see below). For finite changes in state, Eq. (13.10) gives

$$S(T,P) = S(T_0,P_0) + \int_{(T_0,P_0)}^{(T,P)} \frac{C_P}{T}\,dT - V\alpha dP,$$

where the choice of path is unimportant. Note that no change in phase must occur along the path. If not, corrections for the enthalpy change associated with the transition (i.e., the heat) must be included.

With Eq. (13.10), we can finish our discussion of the difference between the heat capacities. In Sec. 8.5.1 of the Thermochemistry chapter we showed that

$$C_P - C_V = \alpha V\left[P + \left(\frac{\partial E}{\partial V}\right)_{N,T} \right], \tag{13.11}$$

cf. Eq. (8.24). But, by choosing a reversible path and keeping N constant, $dE = TdS - PdV$; hence,

$$\left(\frac{\partial E}{\partial V}\right)_{N,T} = T\left(\frac{\partial S}{\partial V}\right)_{N,T} - P = T\left(\frac{\partial S}{\partial P}\right)_{N,T}\left(\frac{\partial P}{\partial V}\right)_{N,T} - P,$$

where the second equality follows from the chain rule. Equation (13.10) gives the entropy derivative, and the pressure derivative is equal to $-1/(V\kappa)$, where κ is the isothermal compressibility. Thus,

$$\left(\frac{\partial E}{\partial V}\right)_{N,T} = \frac{T\alpha}{\kappa} - P \tag{13.12}$$

and

$$C_P - C_V = \frac{VT\alpha^2}{\kappa}.$$

Note that $C_P \geq C_V$ for all materials! Also note that, as expected from Joule's experiments, our last result for $(\partial E/\partial V)_{T,N}$ vanishes for an ideal gas, where $\alpha = 1/T$ and $\kappa = 1/P$.

Express the Joule-Thompson coefficient in terms of α, κ, and C_P/V and verify that it vanishes for an ideal gas.

13.3. Appendix: Proof of Green's Theorem in the Plane

THEOREM:

Consider the differential form:

$$df \equiv M(x, y)dx + N(x, y)dy. \tag{A.1}$$

If M and N have continuous first partial derivatives at all points of some open rectangle, the differential form, Eq. (A.1), is exact at each point of the rectangle if and only if the condition

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \tag{A.2}$$

is satisfied throughout the rectangle. When this holds, the function f(x,y) is given by the line integral

$$f(x, y) = \int_C M(s, t)ds + N(s, t)dt \tag{A.3}$$

along the path from (a,b) to (x,y) shown in Fig. 13.1.

Proof:

The necessity of the condition is shown by noting that if f is exact, then

$$\left(\frac{\partial f}{\partial x}\right)_y = M(x, y)$$

and

$$\left(\frac{\partial f}{\partial y}\right)_x = N(x, y).$$

However, if the second partial derivatives of a function are continuous then the order of differentiation is immaterial and

$$\frac{\partial^2 f(x, y)}{\partial x \partial y} = \frac{\partial^2 f(x, y)}{\partial y \partial x},$$

which when expressed in terms of derivatives of M and N gives Eq. (A.2).

To show that the condition is sufficient is slightly more complicated. First, consider a point infinitesimally close to (a,b); i.e., (a+dx,b+dy). In this case, we can make linear approximations for the behaviors of M and N and the function defined on C, f_C becomes

$$\Delta f_C = \int_0^{dx} M(a + s, b)ds + \int_0^{dy} N(a + dx, b + t)dt$$

$$\approx \int_0^{dx}\left[M(a, b) + \left(\frac{\partial M}{\partial x}\right)_{x=a,y=b} s\right]ds + \int_0^{dy}\left[N(a, b) + \left(\frac{\partial N}{\partial x}\right)_{x=a,y=b} dx + \left(\frac{\partial N}{\partial y}\right)_{x=a,y=b} t\right]dt$$

$$= M(a, b)dx + \left(\frac{\partial M}{\partial x}\right)_{x=a,y=b}\frac{dx^2}{2} + \left[N(a, b) + \left(\frac{\partial N}{\partial x}\right)_{x=a,y=b} dx\right]dy + \left(\frac{\partial N}{\partial y}\right)_{x=a,y=b}\frac{dy^2}{2} \qquad \text{(A.4)}$$

which is valid up to terms of third order in dx and/or dy. Next we repeat the preceding argument on the path C' shown in Fig. 13.1. This gives

$$\Delta f_{C'} \approx N(a, b)dy + \left(\frac{\partial N}{\partial y}\right)_{x=a,y=b}\frac{dy^2}{2} + \left[M(a, b) + \left(\frac{\partial M}{\partial y}\right)_{x=a,y=b} dy\right]dx + \left(\frac{\partial M}{\partial x}\right)_{x=a,y=b}\frac{dx^2}{2}. \qquad \text{(A.5)}$$

If f is single-valued, $f_C = f_{C'}$. By equating the right hand sides of Eqs. (A.4) and (A.5) we see that

$$f_C - f_{C'} \approx dxdy\left[\left(\frac{\partial N}{\partial x}\right)_{x=a,y=b} - \left(\frac{\partial M}{\partial y}\right)_{x=a,y=b}\right] \qquad \text{(A.6)}$$

which vanishes if Eq. (A.2) holds. Incidentally, note that the left hand side of Eq. (A.6) is just a line integral around a closed path and the quantity on the right hand side is an approximate surface integral.

Of course, Eq. (A.6) is valid only for (x,y) infinitesimally close to (a,b). For arbitrary paths, and (x,y) we break up the interior of the path into small rectangles as shown in the following figure:

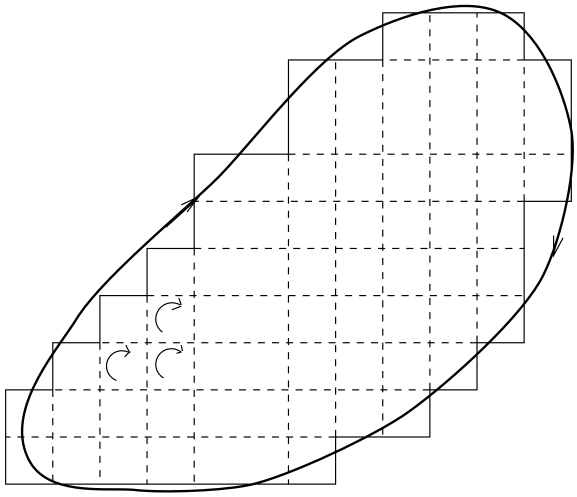


Fig. 13.2.

If the rectangles are small enough, then Eq. (A.6) can be used on each one and the results added together. This leads to cancellations of all the line integrals on the edges of adjacent rectangles inside the path (because of the directions of the integrations) but not those on the edges of the path, and thus finally gives

$$\oint M(x,y)dx + N(x,y)dy = \int\int dxdy\left[\frac{\partial N}{\partial x} - \frac{\partial M}{\partial y}\right].$$

In calculus, this result is called Green's theorem in the plane. Finally, since we've assumed that (A.2) holds,

$$\oint M(x,y)dx + N(x,y)dy = 0 \tag{A.7}$$

which is just what we need to show that f defined by Eq. (13.3) is single-valued (i.e., it is a state function).

14. Thermodynamic Stability: Free Energy and Chemical Equilibrium

14.1. Spontaneity and Stability Under Various Conditions

All the criteria for thermodynamic stability stem from the Clausius inequality, cf. Eq. (8.7.3). In particular, we showed that for any possible infinitesimal spontaneous change in nature,

$$dS \geq \frac{đQ}{T} \ . \tag{14.1}$$

Conversely, if

$$dS < \frac{đQ}{T} \tag{14.2}$$

for every **allowed** change in state, then the system cannot spontaneously leave the current state **NO MATTER WHAT**; hence the system is in what is called stable equilibrium.

The stability criterion becomes particularly simple if the system is adiabatically insulated from the surroundings. In this case, if all allowed variations lead to a decrease in entropy, then nothing will happen. The system will remain where it is. Said another way, the entropy of an adiabatically insulated stable equilibrium system is a maximum. Notice that the term *allowed* plays an important role. For example, if the system is in a constant volume container, changes in state or variations which lead to a change in the volume need not be considered even if they lead to an increase in the entropy.

What if the system is not adiabatically insulated from the surroundings? Is there a more convenient test than Eq. (14.2)? The answer is yes. To see how it comes about, note we can re-write the criterion for stable equilibrium by using the first law as

$$đQ = dE + P_{op}dV - \mu_{op}dN > TdS, \tag{14.3}$$

which implies that

$$dE + P_{op}dV - \mu_{op}dN - TdS > 0 \tag{14.4}$$

for all allowed variations if the system is in equilibrium. Equation (14.4) is the key stability result. As discussed above, if E, V, and N are held fixed $đQ = 0$ and the stability condition becomes $dS < 0$ as before.

What if S,V,N is held constant? From Eq. (14.4), the system will be stable if $dE > 0$; i.e., the energy is a minimum. This has a nice mechanical analogy. Consider a ball rolling on a frictionless parabolic surface in a gravitational field. Clearly, if we place the ball at rest at the lowest point then it will stay there forever. This is the point which minimizes the energy.

Of course, it is not always easy to see how to hold the entropy constant in real experiments. (When is the entropy constant?) A more common situation is when the temperature of the system is held fixed. What is the stability criterion? The problem and its solution are similar to those which led to the introduction of the enthalpy. If (N,T,V) are held fixed, Eq. (14.4) becomes

$$(dE)_{N,T,V} - T(dS)_{N,T,V} > 0, \tag{14.5a}$$

or since T is constant,

$$d(E - TS)_{N,T,V} > 0. \tag{14.5b}$$

Thus, we see that a new state function, $A \equiv E - TS$, is a minimum for a stable equilibrium where (N,T,V) are not allowed to vary. This new state function, is defined via a Legendre transformation on the energy and is called the Helmholtz free energy.

From the definition of A, for a general change in state (i.e., not necessarily with $dT = 0$, etc.)

$$dA = dE - SdT - TdS = (đ\,Q - TdS) + đ\,W - SdT + \mu_{op} dN. \tag{14.6}$$

The Clausius inequality implies that the quantity in the parenthesis is negative (or zero for a reversible process) for any spontaneous change in the state of the system. Moreover, if we consider systems where T and N are held fixed

$$dA \leq đ\,W \quad \text{or} \quad -W \leq -\Delta A. \tag{14.7}$$

This means the $-\Delta A$ is the maximum work you can get out of a process run under constant T and N conditions (hence the name "free energy"). In addition, since A is a state function, you can get the bound without knowing anything about the path (or device)--just by knowing the initial and final states and how to carry out a calculation similar to those we did in thermochemistry.

Since A is a state function, we can always compute changes along reversible paths. In this case,

$$dA = -SdT - PdV + \mu dN. \tag{14.8}$$

In addition, we pick up some new Maxwell relations, e.g.,

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N} = \frac{\alpha}{\kappa}, \tag{14.9}$$

where $\alpha = V^{-1}(\partial V/\partial T)_{P,N}$ is the thermal expansion coefficient and $\kappa = -V^{-1}(\partial V/\partial P)_{T,N}$ is the isothermal compressibility; the last equality follows by using the cyclic rule,

Clearly, there are many different choices of which state variables can be held constant. We will only consider two more. First suppose (S,P,N) is held fixed. This is analogous to what we encountered with the enthalpy. In this case, Eq. (14.4) becomes

$$d(E + PV)_{S,P,N} = (dH)_{S,P,N} > 0 \tag{14.10}$$

for stable equilibrium; i.e., the enthalpy is a minimum.

Finally, and perhaps most importantly, suppose T, P, and N are held fixed. This is the most commonly encountered case. Now Eq. (14.4) becomes

$$d(E + PV - TS)_{T,P,N} > 0. \tag{14.11}$$

Thus a new state function, $G \equiv E + PV - TS = H - TS$, is a minimum for a stable equilibrium with fixed temperature, pressure, and mass. This state function is called the Gibbs free energy.

As was the case with the Helmholtz free energy, ΔG has a direct physical interpretation. From its definition, for a constant (T,P,N) processes,

$$dG = dE - TdS + PdV = (đQ - TdS) + (đW + PdV) \leq (đW + PdV), \tag{14.12}$$

where the last inequality follows from the Clausius inequality. For finite changes in state, we thus find that

$$-W - \int PdV \leq -\Delta G. \tag{14.13}$$

What does this mean? Up to now, we have mainly considered PV work. Of course, there are other kinds (magnetic, electrical but to name two). Hence, $-\Delta G$ provides an upper bound to the non-PV work done by the system on the surroundings (i.e., $-W - \int PdV$) that can be obtained from a constant T,P,N process. If you are manufacturing electric batteries you probably don't care about the amount of PV work which is wasted if the battery expands or contracts--all you want is the electrical work.

As in the case of the Helmholtz free energy, we can consider arbitrary changes in the Gibbs free energy along reversible paths. From its definition

$$dG = -SdT + VdP + \sum_i \mu_i dN_i. \tag{14.14}$$

As before, this gives additional Maxwell relations, for example

$$\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N} = -V\alpha, \tag{14.15}$$

which we obtained in a very complicated way in an earlier section.

As an illustration of the usefulness of Maxwell relations, reconsider our discussion of the Joule-Thompson coefficient:

$$\mu_{JT} = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_{T,N} = -\frac{1}{C_P}\left[T\left(\frac{\partial S}{\partial P}\right)_{T,N} + V\right] = -\frac{V}{C_P}(1 - T\alpha),$$

where the last equality follows by using Eq. (14.15) and the one before that by noting that $dH = TdS + VdP + \mu dN$. Note that the notation often gives a clue where to look for a Maxwell relation. In our example, the entropy derivative is with respect to P, keeping T and N constant. The state function whose natural or canonical variables are T, P, and N is G, and this is where we got the Maxwell relation just used.

One final point, note that the partial molar Gibbs free energy is

$$\bar{G}_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \mu_i, \tag{14.16}$$

where Eq. (14.14) was used. Hence, in a one component system, the Gibbs free energy per mole is just the chemical potential. More generally, $\bar{G}_i$, the partial molar quantity for the i'th component is μ_i, and hence, from Euler's theorem

$$G = \sum_i N_i \mu_i. \tag{14.17}$$

As we discussed earlier, in order that Eqs. (14.17) and (14.14) be consistent, a Gibbs-Duhem relation must hold; i.e.,

$$0 = SdT - VdP + \sum_i N_i d\mu_i, \tag{14.18}$$

which shows that the changes in temperature, pressure and chemical potentials are not all independent.

The various stability results are summarized in the following table.

Criteria for Stable Equilibrium

Held Fixed	State Function	Definition	Differential	Stable Equilibrium Criterion	Simplest Physical Content
Adiabatic* (e.g., E,V,N)	S	$\Delta S = \int \frac{dQ_{rev}}{T}$	$dS = \frac{dQ_{rev}}{T}$	maximum	-
S,V,N	E	$\Delta E = Q + W$	$dE = TdS - PdV + \sum_i \mu_i dN_i$	minimum	$\Delta E_{V,N} = Q_{V,N}$
S,P,N	H	$H \equiv E + PV$	$dH = TdS + VdP + \sum_i \mu_i dN_i$	minimum	$\Delta H_{P,N} = Q_{P,N}$
T,V,N	A	$A \equiv E - TS$	$dA = -SdT - PdV + \sum_i \mu_i dN_i$	minimum	$-W_{T,N} \le -\Delta A_{T,N}$
T,P,N	G	$G \equiv H - TS$	$dG = -SdT + VdP + \sum_i \mu_i dN_i$	minimum	$-W_{non-PV} \le -\Delta G_{P,N}$

*E,N,V implies adiabatic in systems where only PV or chemical work is allowed, the reverse is not true if other kinds or work (e.g., electrical) are possible.

14.2. Examples of free energy calculations

Free energy calculations are carried out in much the same as enthalpy calculations. There are tables of standard free energies of formation of compounds. **Elements in their standard states are assigned zero as their Gibbs free energy of formation.**

Consider the following chemical reaction:

$$H_2(g) + Cl_2(g) \to 2HCl(g).$$

Will the reaction proceed as written under constant T and P conditions? The free energy change is simply

$$\sum \Delta G_f^{(0)}(products) - \Delta G_f^{(0)}(reactants) \tag{14.19}$$

which for the case at hand is just $2\Delta G_f^{(0)}(HCl, g)$ or -184.62 kJ/mol (from Barrow). Hence, a mixture of hydrogen and and chlorine can lower its free energy (by a substantial amount) by reacting to form HCl.

This is an interesting example for another reason; if you mix stoichiometric amounts of H_2 and Cl_2, you will not see any perceptible reaction--the rate of reaction (no matter what the thermodynamics says) is in this case extremely slow. On the other hand, a small amount of light at the right frequency will catalyze the reaction which then proceeds explosively!

Next consider the reaction between graphite and diamond,

$$C(graphite, s) \to C(diamond, s).$$

Now ΔG = 2.90 kJ/mol. The reaction does not proceed as written (too bad). What is perhaps more troubling is that the reverse reaction should proceed spontaneously at STP. (So why invest in diamonds?)

What happens at other temperatures or pressures. To answer this note that from Eq. (14.14), for any compound,

$$\Delta G_f(T, P) = \Delta G_f^{(0)} + \int_{(298K,\ 1\ atm)}^{(T,P)} -S(T, P)dT + V(T, P)dP,$$

where any convenient path can be chosen.

Thus if we raise the pressure,

$$\Delta G_{rxn}(T, P) = \Delta G_{rxn}^{(0)} + \int_{(298K,\ 1\ atm)}^{(298K,P)} \Delta V_{rxn} dP. \tag{14.20}$$

At STP, ΔV_{rxn} = -1.9 cm^3/mol. Hence, increasing the pressure decreases the Gibbs free energy change. If we assume that the molar densities of carbon are roughly independent of pressure, we can calculate the pressure at which the reaction will proceed as written; thus,

$$\Delta G_{rxn}(T, P) \approx 2.90 - 1.9 \times 10^{-9} \Delta P \ (kJ/mol)$$

Hence, the reaction begins to be possible when $P \approx 1.530 \times 10^9 Pa$ or about 15,000 atm.

Similarly, $\Delta S^{(0)}_{rxn} = -3.36 \, J/K \, mol$, hence, keeping the pressure constant and raising the temperature gives:

$$\Delta G_{rxn}(T, P) \approx 2.90 \times 10^3 + 3.36 \, (T - 298.15) \ (J/mol).$$

Hence, raising the temperature only makes graphite more stable (but is good for increasing the rates of reaction). Setting $\Delta G_{rxn} = 0$ gives $T = -565K$, which is clearly impossible. Hence, temperature alone can't be used to change the stable phase of carbon. One caveat, we've approximated $\Delta S^{(0)}_{rxn}$ as independent of temperature. This can't be true at temperatures around absolute zero by the 3rd Law!

14.2.1. Coupled Reactions

In some cases, the direct formation of a certain compound by direct reaction is thermodynamically forbidden. An example is the formation of titanium tetrachloride[1]
from common TiO_2 ore; i.e.,

$$TiO_2(s) + 2Cl_2(g) \rightarrow TiCl_4(l) + O_2(g).$$

It turns out that $\Delta G = +152.3 kJ/mol$. Nonetheless, we can make the reaction go by coupling it to one which pulls it along. For example, suppose we use the produced oxygen to burn carbon; i.e.,

$$C(s, graphite) + O_2(g) \rightarrow CO_2(g),$$

where here $\Delta G = -394.36 kJ/mol$. The free energy change for the coupled processes is -394.36 + 152.3 = -242.1 kJ/mol, and thus the coupled reaction can proceed. The burning carbon supplies the needed free energy to make the desired reaction work. Note that the overall reaction is

$$TiO_2(s) + 2Cl_2(g) + C(s, graphite) \rightarrow TiCl_4(l) + CO_2(g),$$

which also gives $\Delta G = -242.1 kJ/mol$ using the standard calculation.

14.2.2. General Trends

For this discussion, we will consider systems were the reactions take place at a fixed temperature and pressure; as such, the direction of change is determined by

$$\Delta G = \Delta H - T\Delta S,$$

[1] $TiCl_4$ is a precursor used in making pure Ti via the reaction

$$TiCl_4 + 2Mg \rightarrow 2MgCl_2 + Ti \quad \text{or} \quad TiCl_4 + 4Na \rightarrow 4NaCl + Ti$$

it is also used as a catalyst or precusor for various catalysts (e.g., the Ziegler-Natta catalysts).

where ΔH and ΔS are the enthalpy and entropy change for the process, *at the actual temperature and pressure.* As we have said, for constant pressure and temperature processes, $\Delta G < 0$ for the reaction to proceed as written. There can be several ways to arrive at a negative ΔG. For example, ΔG will always be negative if $\Delta H < 0$ and $\Delta S > 0$. On the other hand, if $\Delta H < 0$ and $\Delta S < 0$ then we can expect $\Delta G < 0$ only if T is low enough (this neglects any changes in ΔH and ΔS with temperature). These trends are summarized in the following table:

Constant T & P Process Proceeds as Written

ΔS	ΔH	
	> 0	< 0
< 0	Never	Low enough T*
> 0	High enough T	Always

*Of course, keep in mind that $T > 0$; hence, it is not always possible to find a physical temperature low enough to drive an enthalpy driven reaction. This was the case in our discussion of the graphite/diamond equilibrium

14.3. Chemical Equilibrium

14.3.1. Thermodynamics of Chemically Reacting Systems

A very important example of thermodynamic equilibrium is that of chemical equilibrium at constant pressure and temperature. Consider the following general chemical reaction:

$$2A + B \rightleftarrows 3C + D.$$

The chemical equation imposes a strong constraint on the changes in the numbers of moles of each component; for the forward reaction, each time a mole of B reacts, 2 of A are used up and 3 of C and one of D are produced. Mathematically,

$$\frac{dN_A}{-2} = \frac{dN_B}{-1} = \frac{dN_C}{3} = \frac{dN_D}{1} \equiv d\xi, \tag{14.21}$$

where the extent of the reaction is characterized by the quantity ξ (the Greek letter, pronounced *ksē*) called the progress variable. For an arbitrary chemical reaction involving r chemical components, the last expression generalizes to

$$\frac{dN_1}{\nu_1} = \cdots = \frac{dN_r}{\nu_r} \equiv d\xi, \tag{14.22}$$

where ν_i is the stoichiometric coefficient for the i'th component in the reaction (by convention, it is negative for reactants). This is just a mathematical formulation of the law of definite proportions due to Joseph Proust, 1806, who wrote:

> "I shall conclude by deducing from these experiments the principle I have established at the commencement of this memoir, viz. that iron like many other metals is subject to the law of nature which presides at every true combination, that is to say, that it unites with two constant proportions of oxygen. In this respect it does not differ from tin, mercury, and lead, and, in a word, almost every known combustible."

One can easily relate the actual amounts of compounds present at any stage of the reaction imply by integrating Eq. (14.22); i.e., $N_i = N_i^{(0)} + \nu_i \xi$, where $N_i^{(0)}$ is the amount of compound i present when $\xi = 0$, i.e., at the start of the reaction.

For constant temperature and pressure and total mass (for each element) conditions, the reaction can proceed until the Gibbs free energy is a minimum with respect to all **allowed** variations in the state of the system. By knowing the amounts of the various compounds in terms of ξ it is easy to express the Gibbs free energy in terms of ξ using Euler's theorem (cf. Eq. (14.17)):

$$G(\xi) = \sum_i N_i \left(\frac{\partial G}{\partial N_i} \right)_{T,P,N_{j\neq i}} = \sum_i (N_i^{(0)} + \nu_i \xi)\mu_i,$$

where μ_i is usually a function of ξ as well.

For fixed total mass, temperature, and pressure, the only variations which can be considered are those which change ξ. Hence, we could use the last equation to plot $G(\xi)$ versus ξ; i.e., the reaction moves either to the right or left until $G(\xi)$ is a minimum. Instead of determining the equilibrium point graphically, we can use calculus. We know that G can be a minimum with respect to changes in the progress variable only if

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P,N_{total}} = 0 \tag{14.23}$$

and

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,P,N_{total}} > 0. \tag{14.24}$$

By using the differential form for the change in the free energy together with Eq. (14.22) we find that

$$dG = -SdT + VdP + \sum_{i=1}^{r} \nu_i \mu_i d\xi, \tag{14.25}$$

which when used in Eq. (14.23) gives

$$\Delta\bar{G} \equiv \left(\frac{\partial G}{\partial \xi}\right)_{T,P,N_{total}} = \sum_{i=1}^{r} \nu_i \mu_i = 0 \tag{14.26}$$

at equilibrium. $\Delta\bar{G}$ is called the reaction Gibbs free energy. Since the μ_i are the partial molar Gibbs free energies, Eq. (14.26) is equivalent to $\Delta\bar{G} = 0$. **At equilibrium the free energy change in the reaction per mole vanishes.** (Indeed, this is the principle we applied in the "reaction" between graphite and diamond). From the definition of the Gibbs free energy (G = H -TS), it follows that

$$\Delta\bar{S} = \frac{\Delta\bar{H}}{T}$$

at equilibrium.

What happens if we change temperature or pressure by a small amount? Which way will the equilibrium shift? To answer this, first note the following Maxwell relations:

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N_j} = -\left(\frac{\partial S}{\partial N_i}\right)_{P,T,N_{j\neq i}} = -\bar{S}_i \tag{14.27a}$$

and

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N_j} = \left(\frac{\partial V}{\partial N_i}\right)_{P,T,N_{j\neq i}} = \bar{V}_i \tag{14.27b}$$

which follow from the Gibbs free energy. Thus the changes in the chemical potential associated with temperature or pressure are related to the partial molar entropies or volumes, respectively.

Next consider

$$d(\sum_i \nu_i \mu_i) = \sum_i \nu_i \left(\frac{\partial \mu_i}{\partial T}\right)_{P,N_j} dT + \sum_i \nu_i \left(\frac{\partial \mu_i}{\partial P}\right)_{T,N_j} dP + \left(\frac{\partial (\sum \nu_i \mu_i)}{\partial \xi}\right)_{T,P,N_{total}} d\xi$$

$$= -\Delta \bar{S}\, dT + \Delta \bar{V}\, dP + \left(\frac{\partial \Delta \bar{G}}{\partial \xi}\right)_{T,P,N_{total}} d\xi, \tag{14.28}$$

where, cf. Eqs. (14.27), $\Delta \bar{S} \equiv \sum \nu_i \bar{S}_i$ and $\Delta \bar{V} \equiv \sum \nu_i \bar{V}_i$ are the entropy and volume changes per mole of reaction. Equation (14.28) shows how the free energy change per mole of reaction changes when we change T, P, or ξ.

What happens if we change, T or P in a system where chemical reaction is possible? The progress variable will change until Eq. (14.26) is again valid. Since both the initial and final states satisfy Eq. (14.26), the change in $\Delta \bar{G}$ must vanish; i.e., $d\Delta \bar{G} = d(\sum_i \nu_i \mu_i) = 0$. From Eq. (14.28) this implies that

$$d\xi = \frac{\Delta \bar{S}\, dT - \Delta \bar{V}\, dP}{\left(\frac{\partial \Delta \bar{G}}{\partial \xi}\right)_{T,P,N_{total}}}. \tag{14.29}$$

Moreover, the denominator of the right hand side of the equation is positive, cf. Eqs. (14.24) and (14.26). Equation (14.29) can be rewritten by noting [cf. Eq. (14.26)] that $\Delta \bar{S} = \Delta \bar{H}/T$; i.e.,

$$d\xi = \frac{\frac{\Delta \bar{H}}{T} dT - \Delta \bar{V}\, dP}{\left(\frac{\partial \Delta \bar{G}}{\partial \xi}\right)_{T,P,N_{total}}}. \tag{14.30}$$

Equation (14.30) is a mathematical statement of **LeChatellier's principle**. For reactions which lead to an increase in the volume ($\Delta \bar{V} > 0$), increasing (decreasing) the pressure will shift the equilibrium to the reactant ($d\xi < 0$) [product ($d\xi > 0$)] side of the equation. The reverse is true if the volume change is negative. Similarly, increasing the temperature shifts the equilibrium to the reactant side for reactions which are exothermic ($\Delta \bar{H} < 0$) and to the product side for reactions which are endothermic.

14.4. Chemical equilibria in dilute gases

14.4.1. Chemical Potentials in Pure Materials

For a one-component material, the pressure dependence of the chemical potential (free energy per mole) is easily obtained by integrating Eq. (14.12a); i.e.,

$$\mu = \mu^{(0)}(T) + \int_{P_o}^{P} \bar{V}(T, P')\, dP'.$$

Where $\mu^{(0)}(T)$ is the standard Gibbs free energy of formation at one atm and temperature T, and $\bar{V}(T,P)$ is the molar volume. For solids and liquids, and moderate pressure changes, the molar volume doesn't change much with pressure; hence we will consider it as approximately constant. Thus, **for pure solids and liquids**, we find that

$$\mu \approx \mu^{(0)}(T) + \bar{V}(T)(P - P_o). \tag{14.31a}$$

In gases, on the other hand, the volume changes significantly with pressure. For low enough pressures we can consider the gas to be ideal, and thus, noting V=RT/P, we find that

$$\mu(T,P) = \mu^{(0)}(T) + RT\ln\left(\frac{P}{P_o}\right) = \mu^{(0)}(T) + RT\ln(P), \tag{14.31b}$$

where the second equality follows when $P_o = 1atm$ **and P is the pressure in atmospheres**.

14.4.2. Chemical Potentials in Ideal Gas Mixtures

Our last result can be generalized to gas mixtures if we recall our discussion of Dalton's law of partial pressures. There we considered a gas mixture where one of the components could diffuse in and out of the system through a selective, porous film into a container containing a pure sample of that component. At equilibrium, the pressure in the pure sample was P_i, the partial pressure of the i'th component in the mixture.

If we view the process as the following "chemical reaction"

$$\textit{Component i in mixture} \rightleftarrows \textit{Component i in pure sample}.$$

The equilibrium condition becomes:

$$\mu_{i,mixture}(T,P,x_{1,}\cdots,x_{r-1}) = \mu_{i,pure}(T,P_i) = \mu_i^{(0)}(T) + RT\ln(P_i). \tag{14.32}$$

Hence, the form of the chemical potential in a gas mixture is very similar to that in a pure sample, with the exception that the pressure is not the total pressure of the gas, but is the partial pressure of the component in question.‡

‡ What happens if a selective filter cannot be found for one of the compounds in the gas mixture? Consider a two component gas mixture where only component "1" is known to obey Eq. (14.32). The Gibbs-Duhem relation for a binary mixture, with T and P constant, is $N_1 d\mu_1 + N_2 d\mu_2 = 0$, and can be used to show that

$$-x_2\left(\frac{\partial \mu_2}{\partial x_1}\right)_{T,P} = x_1\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} = RT,$$

where we have divided by $(N_1 + N_2)dx_1$ and used Eq. (14.32) with $P_1 = Px_1$ for μ_1. Since $x_2 = 1 - x_1$, the chain rule can be used to rewrite the last result as

$$\left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} = \frac{RT}{x_2}.$$

This can be integrated, giving

Knowing this, we are ready to discuss chemical equilibria in gases. From Eq. (14.26), the equilibrium condition becomes:

$$0 = \sum_i \nu_i \mu_i^{(0)}(T) + RT \ln(P_1^{\nu_1} P_2^{\nu_2} \cdots P_r^{\nu_r}) \tag{14.33}$$

or

$$P_1^{\nu_1} P_2^{\nu_2} \cdots P_r^{\nu_r} = K_P(T) \equiv \exp\left[-\sum \nu_i \mu_i^{(0)}(T)/RT\right] = e^{-\Delta \bar{G}^{(0)}/RT}, \tag{14.34}$$

where $K_P(T)$ is called the pressure equilibrium constant. Notice that it is only a function of temperature, the stoichiometric coefficients, and properties of the pure (i.e., unmixed) gases.

We can use Dalton's law of partial pressures to reexpress Eq. (14.33b) in terms of concentrations or mole fractions. For example, since $[i] = N_i/V = P_i/RT$, substitution into Eq. (14.33b) gives

$$[1]^{\nu_1}[2]^{\nu_2} \cdots [r]^{\nu_r} = \frac{e^{-\Delta \bar{G}^{(0)}/RT}}{(RT)^{\sum \nu_i}} \equiv K_c(T). \tag{14.35}$$

Similarly, since $P_i = Px_i$, where x_i is the mole fraction of i and P is the total pressure, we have

$$x_1^{\nu_1} x_2^{\nu_2} \cdots x_r^{\nu_r} = \frac{e^{-\Delta \bar{G}^{(0)}/RT}}{P^{\sum \nu_i}} \equiv K_x(T). \tag{14.36}$$

One final point. In the preceding examples, we've assumed that all the compounds are gases, and hence, have used Eq. (14.31b) for the chemical potentials. Should one or more of the components be in a condensed (strictly speaking, pure) phase, e.g., solid or liquid, then we would have to use Eq. (14.31a) instead. Moreover, since the molar volumes of liquids and gases are small, we can ignore the pressure term in Eq. (14.31a) as long as the $P - P_o$ isn't too large. For our discussion of equilibrium constants, this has one consequence; namely, the condensed phase components drop out of stoichiometric quotient. Note that this is not true for solutions.

14.5. Examples of Chemical Equilibrium Calculations

14.5.1. Determination of Free Energies of Formation

There are a number of ways in which to measure the standard free energies of formation of a compound. Consider the formation of ammonia,

$$\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \rightleftarrows NH_3(g),$$

$$\mu_2 = \mu_2^* + RT \ln(x_2).$$

μ_2^* is known as the "apparent free energy" and becomes the standard one, $\mu_2^{(0)}$, if we can let $x_1 \to 0$, i.e., almost pure "2", and still have "1" obey Eq. (14.32). This is easy to ensure for gas mixtures, but can be problematic in solutions.

at STP. The free energy change for the reaction is $\Delta G_f^{(0)}(NH_3, g)$. If we measure the equilibrium constant,

$$\frac{P_{NH_3}}{P_{N_2}^{1/2} P_{H_2}^{3/2}} = e^{-\Delta G_f^{(0)}(NH_3,g)/RT}, \tag{14.37}$$

then we can easily compute the free energy of formation of ammonia.

14.5.2. Determination of the Extent of a Reaction

Reconsider the reaction

$$N_2O_4(g) \rightleftarrows 2NO_2(g).$$

The extent of the reaction is easily measured by measuring the apparent deviation from the ideal gas law. As before, let α be the fraction of N_2O_4 dissociated. If there were N_0 moles of N_2O_4 initially, then there are $(1-\alpha)N_0$ and $2\alpha N_0$ moles of N_2O_4 and NO_2 at equilibrium, respectively. The corresponding partial pressures can be computed from Dalton's law.

When the result is used in the equilibrium constant condition we find that

$$K_P = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{4\alpha^2}{1-\alpha}\ \frac{N_0 RT}{V} = \frac{4\alpha^2 P}{1-\alpha^2}, \tag{14.38}$$

where P is the total pressure on the system. This can be solved for the fraction dissociated, with the result that

$$\alpha = \left(\frac{K_P}{K_P + 4P}\right)^{1/2}$$

Thus, if we calculate the equilibrium constant from a table of free energies, the degree of dissociation is easily found. Note that the result depends on both T and P. From tables of standard enthalpies of formation (Castellan), $\Delta\bar{H}^{(o)} = 2 \times 33.18 - 83.7 = -17.3\, kJ/mol < 0$ and $\Delta\bar{V} = 2\bar{V}_{NO_2} - \bar{V}_{N_2O_4} = RT/P > 0$, assuming ideal gases. Hence, according to LeChatellier's principle we expect that the reaction should shift to the left (i.e., less dissociation) as pressure is increased. Our final equation for α shows this. For this reaction, as we shall see in the next section, $K_P(T)$ decreases as temperature increases, which when used with our expression for α is again consistent with LeChatellier's principle.

14.5.3. Temperature Dependence of K_P

The equilibrium constant, K_P, is only a function of the temperature. From its definition, cf. Eq. (14.34),

$$\frac{d\ln(K_P)}{dT} = -\frac{d(\Delta\bar{G}^{(0)}/RT)}{dT} = -\frac{1}{RT^2}\left(T\ \frac{d(\Delta\bar{G}^{(0)})}{dT} - \Delta\bar{G}^{(0)}\right) = \frac{T\Delta\bar{S}^{(0)} + \Delta\bar{G}^{(0)}}{RT^2} = \frac{\Delta\bar{H}^{(0)}}{RT^2},$$

(14.39)

where the second to last equality follows when Eqs. (14.27a) and (14.34) are used. This is known as the Gibbs-Helmholtz equation. Thus, by integrating we find that

$$\ln\left[\frac{K_P(T_2)}{K_P(T_1)}\right] = \int_{T_1}^{T_2} \frac{\Delta\bar{H}^{(0)}}{RT^2}\, dT \approx \frac{\Delta\bar{H}^{(0)}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \tag{14.40}$$

The last equality in Eq. (14.40) follows if we assume that $\Delta\bar{H}^{(0)}$ is approximately constant with respect to temperature, or equivalently, that $\Delta\bar{C}_P \approx 0$ (which also implies that $\Delta\bar{S}^{(0)}$ is constant. Why?). Indeed, with this approximation, Eq. (14.40) simply states that

$$\frac{K_P(T_2)}{K_P(T_1)} = \exp\left(-\frac{\Delta\bar{G}^{(0)}(T_2)}{RT_2} + \frac{\Delta\bar{G}^{(0)}(T_1)}{RT_1}\right), \tag{14.41}$$

where $\Delta\bar{G}^{(0)}(T) = \Delta\bar{H}^{(0)} - T\Delta\bar{S}^{o}$, as usual. Finally, note, that as in our discussion of LeChatellier's principle, the equilibrium will shift to the product side, i.e., K_P increases, when the temperature is raised if $\Delta\bar{H}^{(0)} > 0$.

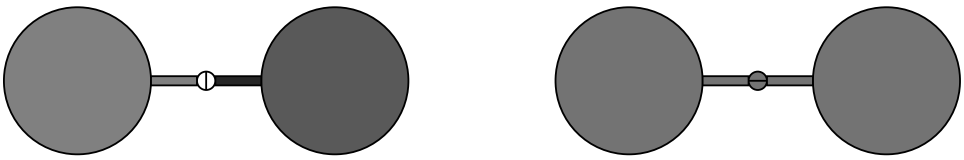
There is a simple graphical way in which to apply the Gibbs-Helmholtz equation. By expressing Eq. (14.39) as a differential, it follows that

$$d\ln(K_P) = \frac{\Delta\bar{H}^{(0)}}{RT^2}\, dT = -\frac{\Delta\bar{H}^{(0)}}{R}\, d\left(\frac{1}{T}\right);$$

hence, plotting $\ln(K_P)$ versus $1/T$ will give a curve whose slope at any point is $-\Delta\bar{H}^{(0)}/R$, and to the extent that $\Delta\bar{H}^{(0)}$ is independent of temperature, will give a straight line. This is a powerful way to determine enthalpy (and entropy) changes without having to do calorimetry.

14.5.4. Free Energy and Entropy of Mixing

Perhaps the simplest process is one where two samples of different pure gases are isothermally mixed as depicted in the figure below



A(P,T,V) + B(P,T,V) $\longrightarrow$ A+B (P,T,2V)

As you might expect, this process always occurs spontaneously. The total pressure[‡] and temperature remain constant during the process (at least for an ideal gas). What is the Gibbs free energy

[‡]For this to happen, it is necessary that the pressures in the unmixed state be identical; hence,

$$\frac{P}{RT} \equiv \frac{N_A}{V_A} \equiv \frac{N_B}{V_B} = \frac{N_A + N_B}{V_A + V_B},$$

change?

From Eq. (14.32), it follows that the free energy of the final state is

$$G_{final} = N_1\left[\mu_1^{(0)}(T) + RT\ln(P_1)\right] + N_2\left[\mu_2^{(0)}(T) + RT\ln(P_2)\right]. \tag{14.42}$$

Similarly, the Gibbs free energy of either of the pure samples is

$$G_i = N_i\left[\mu_i^{(0)}(T) + RT\ln(P)\right] \tag{14.43}$$

and hence, the free energy of mixing per mole of mixture, $\Delta\bar{G}_{mix}$, is

$$\Delta\bar{G}_{mix} = RTx_1\ln(x_1) + RTx_2\ln(x_2), \tag{14.44}$$

where x_i is the mole fraction of i and where Dalton's law of partial pressures, $P_i = Px_i$, was used. It is easy to generalize this result to arbitrary mixtures of ideal gases

$$\Delta\bar{G}_{mix} = RT\sum_i x_i\ln(x_i). \tag{14.45}$$

Since $0 < x_i < 1$, the free energy change is negative and the mixing occurs spontaneously.

Equation (14.45) can be used to calculate the entropy and enthalpy of mixing. By using Eq. (14.14) it follows that

$$\Delta\bar{S}_{mix} = -\left(\frac{\partial\Delta\bar{G}_{mixing}}{\partial T}\right)_{P,x_i}, \tag{14.46}$$

which when used in Eq. (14.45) gives

$$\Delta\bar{S}_{mix} = -R\sum_i x_i\ln(x_i) > 0. \tag{14.47}$$

Moreover, since

$$\Delta\bar{H}_{mix} = \Delta\bar{G}_{mix} + T\Delta\bar{S}_{mix}, \tag{14.48}$$

it follows that the heat of mixing associated with the mixing of ideal gases is zero. **No heat is absorbed or released for the mixing of ideal gases.** The process is driven entirely by entropy. As we shall see next term, a similar result holds for the mixing of dilute solutions. Similarly, note that there is no volume change for mixing ideal gases (see Eq. (14.14) and take a pressure derivative). In a binary mixture, what composition has the most negative free energy of mixing?

---

where the first two equalities are conditions on the initial state, while the last one follows from the preceding two.

15. Thermodynamic Stability

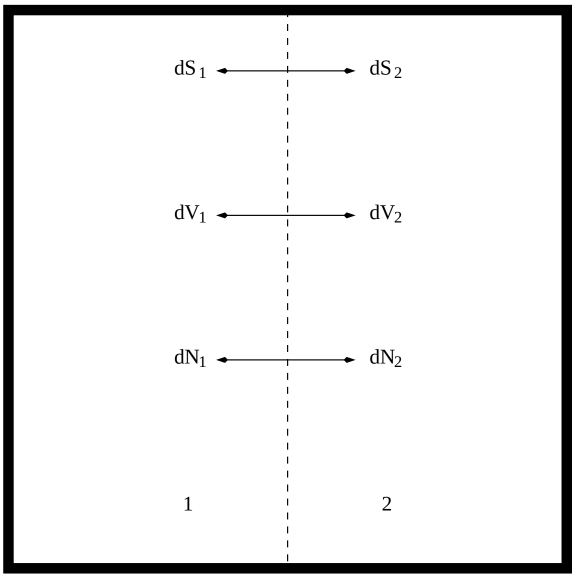


Fig. 15.1. An isolated system considered as two subsystems, each exchanging heat (entropy, if reversible), volume, and mass with each other.

The fact that the overall state functions must be minima (E,H,A,G) or maxima (S) at equilibrium under specified conditions has some interesting consequences. For example, consider reversible changes system with constant S, V and N_i. As we showed earlier the energy of the entire system is a minimum at equilibrium under these conditions. It is important to realize that we are talking about the total S, V and N_i for the system (viewed as a black box). Nothing is implied for the local values of (S, V, N_i), and in particular, if we imagine that the system is split into two subsystems, internal processes of the type shown in Fig. 15.1 are completely allowed, provided that

$$dS_1 + dS_2 = 0, \tag{15.1a}$$

$$dV_1 + dV_2 = 0, \tag{15.1b}$$

and

$$dN_1 + dN_2 = 0 \quad \text{for each component.} \tag{15.1c}$$

Given that

$$dE_{total} = dE_1 + dE_2, \tag{15.2}$$

where, as usual,

$$dE_i = T_i dS_i - P_i dV_i + \mu_i dN_i, \tag{15.3}$$

we have, using Eqs. (15.1a)-(15.1c),

$$dE_{total} = (T_1 - T_2)dS_1 - (P_1 - P_2)dV_1 + (\mu_1 - \mu_2)dN_1. \tag{15.4}$$

Since the total energy system of our must be a minimum at equilibrium, and the dS_1, dV_1 and dN_1 are arbitrary (and in particular can have any sign), we see that E_{total} can be a minimum only if $dE_{total} = 0$, which in turn requires that

$$T_1 = T_2, \;\; P_1 = P_2 \;\text{ and }\; \mu_1 = \mu_2; \tag{15.5}$$

i.e., the temperature, pressure and chemical potentials must be uniform. Note that this requires that the exchanges depicted in Fig. 15.1 are possible. Should the system be composed of two sub-parts that are, for example, thermally insulated then $dS_1 = dS_2 = 0$ and these parts can equilibrate with different temperatures, etc..

Our result in Eq. (15.5) only guarantees that the total energy is an extremum. Consider the entropy dependence of the energies. By using a Taylor expansion in entropy, we have

$$dE_i = TdS_i + \frac{1}{2}\left(\frac{\partial^2 E}{\partial S^2}\right)_{V,N} dS_i^2 + \ldots \tag{15.6}$$

which when used in Eqs. 2-5, shows that the second order energy change is

$$dE^{(2)}_{total} = \frac{1}{2}\left(\frac{\partial^2 E}{\partial S^2}\right)_{V,N} (dS_1^2 + dS_2^2), \tag{15.7}$$

which must be positive if the total energy is a minimum (this is just the usual second derivative test you learned in calculus). In turn, this implies that

$$\left(\frac{\partial^2 E}{\partial S^2}\right)_{V,N} = \left(\frac{\partial T}{\partial S}\right)_{V,N} = \frac{T}{C_V} > 0; \tag{15.8}$$

i.e., $C_V > 0$. This same reasoning can be applied to the dV and dN contributions.

More generally, we must consider the possibility that multiple internal processes are taking place simultaneously. By generalizing the Taylor expansion to functions of more than one variable it follows that

$$dE_i^{(2)} \equiv \frac{1}{2}\left(\frac{\partial^2 E}{\partial S^2}\right)_{V,N} dS_i^2 + \left(\frac{\partial^2 E}{\partial S \partial V}\right)_{N} dS_i dV_i + \frac{1}{2}\left(\frac{\partial^2 E}{\partial V^2}\right)_{S,N_i} dV_i^2 + \ldots \tag{15.9}$$

was positive, where terms involving changes of N_i have been dropped. Moreover, by using the expressions for the derivatives of the internal energy, Eq. (15.9) can be rewritten as:

$$dE_i^{(2)} \equiv \frac{T}{2C_V} dS_i^2 + \left(\frac{\partial T}{\partial V}\right)_{S,N_i} dS_i dV_i - \frac{1}{2}\left(\frac{\partial P}{\partial V}\right)_{S,N_i} dV_i^2 + \ldots, \tag{15.10}$$

or in matrix notation:

$$dE_i^{(2)} = \frac{1}{2}\begin{bmatrix} dS_i \\ dV_i \end{bmatrix}^\dagger \cdot \begin{bmatrix} \dfrac{T}{C_V} & \left(\dfrac{\partial T}{\partial V}\right)_{S,N_i} \\ \left(\dfrac{\partial T}{\partial V}\right)_{S,N_i} & -\left(\dfrac{\partial P}{\partial V}\right)_{S,N_i} \end{bmatrix} \cdot \begin{bmatrix} dS_i \\ dV_i \end{bmatrix} \tag{15.11}$$

which must be positive for arbitrary dS_i and dV_i.

The matrix in Eq. (15.11) is symmetric and the expression on the right hand side of Eq. (15.11) is known as a symmetric bi-linear form. From linear algebra, we know that symmetric matrices can be diagonalized; i.e., a basis in the $[dS_i, dV_i]$ space can be found where the matrix elements are zero except for the diagonal ones which are equal to the eigenvalues (denoted as $\lambda_\pm$). In this basis, Eq. (15.11) becomes

$$dE_i^{(2)} = \frac{1}{2}\,(\lambda_+ dc_+^2 + \lambda_- dc_-^2), \tag{15.12}$$

where $dc_\pm$ are the expansion coefficients of $[dS_i, dV_i]$ in the special basis.

In order that the right hand side of Eqs. (15.3) or (15.12) positive for all possible variations of the system, it is necessary and sufficient that the eigenvalues of the matrix, $\lambda_\pm$, be positive. They satisfy the characteristic equation, i.e.,

$$0 = \lambda_\pm^2 - \lambda_\pm\left[\frac{T}{C_V} - \left(\frac{\partial P}{\partial V}\right)_{S,N_i}\right] - \frac{T}{C_V}\left(\frac{\partial P}{\partial V}\right)_{S,N_i} - \left(\frac{\partial T}{\partial V}\right)_{S,N_i}^2. \tag{15.13}$$

This quadratic equation is easily solved and follows that in order that the eigenvalues be positive,

$$C_V > 0, \tag{15.14a}$$

$$-\left(\frac{\partial P}{\partial V}\right)_{S,N_i} > 0, \tag{15.14b}$$

and

$$\left(\frac{\partial T}{\partial V}\right)_{S,N_i}^2 < -\frac{T}{C_V}\left(\frac{\partial P}{\partial V}\right)_{S,N_i}. \tag{15.14c}$$

The inequality in Eq. (15.14a) is just what we obtained earlier. That in Eq. (15.14b) implies that the adiabatic compressibility (cf. Problem Set 5),

$$\kappa_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,N},$$

is positive.

The analysis for variations involving the number of moles of a given species follows in exactly the same manner.

16. Entropy & Randomness

As was mentioned in class, it is possible to give a simple quantitative microscopic derivation of the expression for the entropy of mixing for an ideal solution or ideal gas mixture. To begin, consider the following simple lattice model for the system:

1	1	8	1	1	8	1	8
1	2	4	3	8	1	8	4
1	2	8	1	8	8	8	2
1	8	7	5	2	7	3	8
1	6	2	7	4	4	8	2
8	3	8	1	8	8	1	8

Fig. 16.1. Each cell is labeled according to the kind of molecule it contains.

The volume occupied by the mixture has been divided into M equivalent cells, and each is randomly occupied by a single molecule of a given type in the system. Let N_i be the number of molecules of the i'th species (the "solvent" counts as a species).

How many states are available for the system in this model? Specifically, how many ways can the molecules occupy the cells? Consider species 1: The first molecule can choose M cells, the second M-1, etc.. Finally, the last species 1 molecule can choose $M-N_1-1$ different cells to occupy. Thus the number of ways of assigning the species 1 molecules to the cells is

$$M(M-1)\cdots(M-N_1-1) \equiv \frac{M!}{(M-N_1)!}\,, \tag{16.1}$$

where $N! = N(N-1)(N-2)\cdots 1$ is called the factorial function.

The other species must still be added to the lattice. Consider species 2. Now there are only $M - N_1$ cells to choose from; by repeating the preceding argument, it is easy to show that the number of ways of adding species 2 is

$$\frac{(M-N_1)!}{(M-N_1-N_2)!}\,. \tag{16.2}$$

The total number of ways of adding both species 1 and species 2 to the lattice is the product of the ways of adding each; i.e.,

$$\frac{M!}{(M - N_1 - N_2)!} \,. \tag{16.3}$$

Finally, we can repeat the argument until the entire lattice is filled. The total number of ways of adding the molecules to the system is

$$M!. \tag{16.4}$$

Does each of these ways correspond to a state of the system? The answer is no, not because we have made an error in our calculation, but because we have ignored a basic property of nature; namely, the Heisenberg Uncertainty Principle. Equation (16.4) would be correct if we could distinguish the different molecules of each species. The uncertainty principle makes this impossible, and thus each state of the system cannot depend on which of the equivalent molecules are in the specific cells -- it is impossible to tell.

Thus Eq. (16.4) over-counts the number of **different** states available to the system. By how much? Again consider species 1. After the N_1 cells are chosen one still has the freedom to permute species 1 molecules between the different chosen cells; there are $N_1!$ ways of permuting the species 1 molecules, and these permutations are included in Eq. (16.1). However, as we have just argued, quantum mechanics makes these permutations irrelevant to the calculation of the number of inequivalent states available to the system, and hence, Eq. (16.1) should be divided by the number of ways of rearranging the equivalent molecules on the same set of lattice cells. By repeating this argument for all species, it follows that the number of inequivalent states of the system are:

$$\frac{M!}{N_1!N_2!\cdots} \,. \tag{16.5}$$

The calculation of the entropy of mixing now follows by using the statistical (Boltzmann) expression for the entropy:

$$S = k_B \ln(\textit{number of states}), \tag{16.6}$$

where k_B is Boltzmann's constant ($k_B = R/N_A = 1.38 \times 10^{-23} J\ K^{-1}$). By using Eq. (16.5) in Eq. (16.6), we obtain

$$\Delta S_{mixing} = k_B \left[\ln(M!) - \sum_i \ln(N_i!) \right]. \tag{16.7}$$

This still doesn't look like the expression we obtained in class. Note, however, that the factorials which appear in Eq. (16.7) are factorials of huge numbers ($\approx 10^{23}$). There is an accurate approximation for the natural logarithm of a large factorial known as Stirling's formula, specifcally,

$$\ln(N!) \approx N[\ln(N) - 1] \tag{16.8}$$

(try it for N=50). If Eq. (16.8) is used in Eq. (16.7) and we remember that $M = \sum_i N_i$, a little algebra shows that

$$S_{mixing} = -k_B \sum_i N_i \ln\left(\frac{N_i}{M}\right). \tag{16.8}$$

Since, x_i, the mole fraction of species i is

$$\frac{N_i}{M},$$

Eq. (16.8) is equivalent to the expression we obtained by examining ideal gas mixtures that obey Dalton's law or, as you will see, solutions that obey Raoult's Law or. (Recall that the gas constant $R = k_B N_A$, where N_A is Avogadro's number).

17. Electrochemical Cells

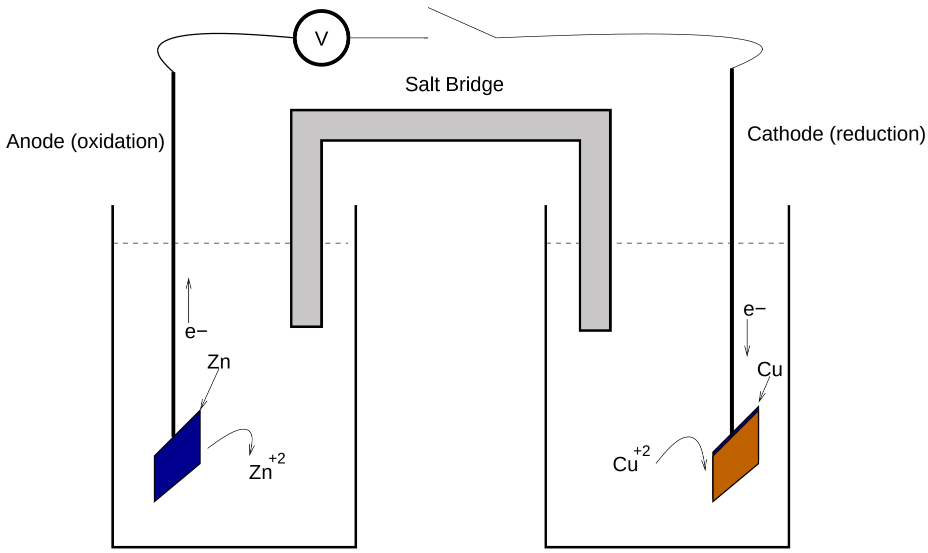


Fig. 17.1. The Galvanic or Daniels cell. Oxidation occurs at the anode, while reduction occurs at the cathode. For the compounds shown, the abbreviated cell reaction is $Zn|Zn^{+2}||Cu^{+2}|Cu$**.**

17.1. General Considerations

Figure 17.1 shows a simple device used that functions as a battery, the so-called Galvanic or Daniels cell. Basically, when the switch is closed, the zinc electrode will oxidize, loosing 2 electrons per atom, and producing a zinc ion. These travel through the external circuit (doing work), and reenter the cell at the cathode, where one copper ion is reduced to copper metal. Thus, we can describe the redox chemistry in terms of the half-reactions:

$$Zn \to Zn^{+2} + 2e^{-} \quad \text{(at the anode)}$$

$$Cu^{+2} + 2e^{-} \to Cu \quad \text{(at the cathode)}$$

and

$$Zn + Cu^{+2} \to Zn^{+2} + Cu \quad \text{(overall).}$$

Note that the reaction leads to a net charge imbalance in the cell and this is restored by having the counter-ions of the salts diffuse as needed through the salt-bridge.

The first question to answer is key; namely, how much work can be obtained per mole of reaction in this cell? At least under constant T and P conditions this can be answered by recalling that

$$-W_{non-PV} \le -\Delta G_{rxn}$$

or

$$-đ W_{non-PV} \le -d\Delta G_{rxn} = -\sum_i \nu_i \mu_i d\xi = -\Delta\bar{G}_{rxn} d\xi, \tag{17.1}$$

where $-W_{non-PV}$ is just the non-mechanical (here electrical) work being done by the system on the surroundings, and where the inequality becomes an equality when the process is reversible. Indeed, one can come close to having the cell operate reversibly by having very little current run through the external circuit. Equation (17.1) is just what we saw when we used the law of definite proportion in chemical reactions.

In electrical terms, suppose there is a voltage difference, $\Delta\mathcal{E}$, between the two electrodes[1]. Thus, by definition, each electron will change its energy by $-e\Delta\mathcal{E}$ as it moves through the external circuit (remember, by convention, electrons have negative charge). Equivalently, they do $e\Delta\mathcal{E}$ *electrical* work on the surroundings. Hence, by using Eq. (17.1) we see that

$$\Delta\mathcal{E} \le -\frac{\Delta\bar{G}_{rxn}}{nF}, \tag{17.2}$$

where n is the number of moles of electrons transferred in the reaction (2 for our example above), $-F \equiv -N_A e$ is the charge associated with one mole of electrons, and is known as the Faraday; It has the value

$$F = 96{,}487 \text{ coul/mol} \;\text{ or } 2.891 \times 10^{14} \text{ esu/mol.}$$

Henceforth, we will restrict our discussion to reversible cells, in which case Eq.(17.2) becomes an equality. Notice that the cell EMF is independent of the precise way you balance the overall reaction. Actually, the main thing that is important in balancing the redox reactions given above is that we produce the same number of electrons in the oxidation at the anode as are consumed in the reduction at the cathode. Lets write the free energy change for each half-reaction as

$$\Delta G_{half-reaction} = \mp nF\Delta\mathcal{E}_{half-reaction},$$

where we'll use the - sign for reductions and the + sign for oxidations, i.e., we define the half-reaction potentials for reductions; hence, for our example,

$$-\Delta G_{rxn} = 2F\Delta\mathcal{E}_{rxn} = 2F\left(\Delta\mathcal{E}_{Cu^{+2}|Cu} - \Delta\mathcal{E}_{Zn^{+2}|Zn}\right).$$

For the reaction to proceed as written when the circuit is closed, we need $\Delta G_{rxn} \le 0$, or equivalently, $\Delta\mathcal{E} \ge 0$. If we assume standard state conditions, we can simply look up the reduction potentials in a table, which for our reaction has

[1]For historical reasons, this is also known as the electromotive force or EMF.

Standard Reduction Potentials

Half Reaction	$\Delta\mathcal{E}$ (Volts, V)
$Zn^2 + 2e^- \to Zn$	-0.763
$Cu^2 + 2e^- \to Cu$	0.337

Hence, the overall cell EMF is $0.337 - (0.763) = 1.100V$ and the cell operates as written. Note that the standard state for electrochemical reactions is defined not with respect to elements in their standard states, but rather, against a standard electrode, the so-called standard hydrogen electrode (SHE).

What happens if the conditions aren't standard? We can still get an expression for the reversible cell EMF from Eqs. (17.1) and (17.2) if we know what the chemical potentials are. Recall that we have

$$\mu_i = \mu_i^{(0)} + RT\ln(a_i), \tag{17.3}$$

where a_i is the activity of compound i; it is the partial pressure in *atm* for ideal gases, or the molar concentration in ideal solutions, but otherwise is more complicated. When the steps leading to Eq. (17.2) are repeated it follows that

$$\Delta\mathcal{E} \le \Delta\mathcal{E}^{(0)} - \frac{RT}{nF}\ln(a_1^{\nu_1}\cdots a_r^{\nu_r}) = \Delta\mathcal{E}^{(0)} - \frac{0.05916}{n}\log_{10}(a_1^{\nu_1}\cdots a_r^{\nu_r}), \tag{17.4}$$

where $\Delta\mathcal{E}^{(0)}$ is the standard cell EMF, as calculated above, the term with the logarithm accounts for any non-standard conditions and the last equality is what you get at 20C, converting to base-10 logarithms. This is known as the Nernst equation.

17.2. Concentration Cells

One useful application of the Nernst equation and galvanic cells is the so-called concentration cell. Here, both cells contain the same metal/ion pairs, just the concentrations are different, e.g.,

$$Ag|Ag^+(a_{anode})||Ag^+(a_{cathode})|Ag,$$

where $a_{anode/cathode}$ are the activities (molar concentration for ideal solutions) in each cell. For this system, $\Delta\mathcal{E}^{(0)} = 0$, and thus

$$\Delta\mathcal{E} = -\frac{RT}{nF}\ln\left(\frac{a^{\nu}_{cathode}}{a^{\nu}_{anode}}\right),$$

where $n = \nu = 1$ for the $Ag|Ag^+$ example. If one of the cells is a standard solution, a simple electrical measurement and application of the last equation gives the activity (molar concentration) of the other. This is the basic idea behind things like pH meters etc. Note that for really accurate work, the role of the salt bridge must be considered more carefully, something not considered here.

17.3. Connection to Equilibrium Constants

If we run the cell until the system is at equilibrium the EMF will be zero, hence, by using the Nernst equation, it follows that

$$a_1^{v_1} \cdots a_r^{v_r} = K = e^{nF\Delta\mathcal{E}^{(0)}/RT}, \tag{17.5}$$

where gives another connection between equilibrium constants and thermodynamic quantities.

Again, voltage is easy to measure very accurately, and this is a good way to measure concentration effects etc. on equilibrium.

17.4. Temperature effects

By using the basic relation between the cell EMF and the Gibbs free energy change, it follows that

$$\left(\frac{\partial\Delta\mathcal{E}}{\partial T}\right)_P = -\frac{1}{nF}\left(\frac{\partial\Delta\bar{G}_{rxn}}{\partial T}\right)_P = \frac{\Delta\bar{S}_{rxn}}{nF}\,. \tag{17.6}$$

If we assume that $\Delta\bar{S}_{rxn}$ is independent of temperature (i.e., $\Delta\bar{C}_P$ is small), we can integrate Eq. (17.6), to give

$$\Delta\mathcal{E}(T) \approx \Delta\mathcal{E}(T_0) + \frac{\Delta\bar{S}_{rxn}}{nF}(T - T_0). \tag{17.7}$$

Note that for many redox reactions $\Delta\bar{S}_{rxn}$ is small (less than 50J/K). This leads to only $10^{-5} - 10^{-4}$ V/K change in $\Delta\mathcal{E}$; hence, the cell EMF is relatively insensitive to temperature. Finally, by noting that at constant temperature, $\Delta\bar{H} = \Delta\bar{G} + T\Delta\bar{S}$, and using Eq. (17.6), we see that

$$\Delta\bar{H} = -nF\left[\Delta\mathcal{E} - T\left(\frac{\partial\Delta\mathcal{E}}{\partial T}\right)_P\right], \tag{17.8}$$

or equivalently,

$$\left(\frac{\partial\Delta\mathcal{E}/RT}{\partial T}\right)_P = \frac{\Delta\bar{H}}{nFRT^2}\,, \tag{17.9}$$

which is basically the Gibbs-Helmholtz equation introduced earlier.

18. Problem Sets

Note that the due dates are last year's. This year's will be announced in class and on the web site.

18.1. Problem Set 1

DUE: Friday, September 25, 2015

1. a) In a one-component system, if $\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N}$, show that $\alpha = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_{P,N}$, where $\rho \equiv N/V$ is the molar density. Note, show this for an arbitrary material, do *not* assume that the system is an ideal gas!

b) More generally, show that

$$\frac{d\rho}{\rho} = -\alpha dT + \kappa dP,$$

where $\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$ is the isothermal compressibility.

c) At 25^oC a sealed, rigid container is completely filled with liquid water. If the temperature is raised by 10C, what pressure will develop in the container? For water, $\alpha = 2.07 \times 10^{-4}/K$ and $\kappa = 4.50 \times 10^{-5}/atm$. Note: Do **not** use the ideal gas equation in a)-c).

2. Use the van der Waals equation and complete the derivation of the relationship between the a and b parameters and the critical pressure, temperature and molar volume, i.e., p_c, T_c and $\bar{V}_c$, respectively.

3. (Castellan, problem 3.3) The critical constants for water are 374^oC, 22.1 MPa, and 0.0566 L/mol (*be careful with units here*). Calculate values of a, b, and R using the van der Waals equation's expressions for the critical constants and compare the value of R with the correct value. Compute the constants a and b from p_c and T_c (and the correct value of R. Finally, using these values, compute the critical volume and compare with the experimental value. What is all this telling you?

4. (Castellan, problem 4.2)

a) Compare the average speed of an oxygen molecule with that of a molecule of carbon tetrachloride at 20^oC;

b) Compare their average kinetic energies.

5. (Castellan, problem 4.5) An oxygen molecule having the average velocity at 300^oK is released from the earth's surface to travel upward. If it could move without colliding with other molecules, how high would it go before coming to rest? How high could it go if it had the average kinetic energy?

18.2. Problem Set 2

DUE: Monday, October 19, 2015

1.

a) Derive the expression for the most probable speed in a gas.

b) Another way to characterize the width of a probability distribution is to compute the standard deviation, σ. Calculate σ for the *speed* distribution; i.e.,

$$\sigma \equiv \sqrt{< (c - < c >)^2 >}.$$

(HINT: you may find the calculation easier if you first show that $< (c - < c >)^2 > = < c^2 > - < c >^2$).

c) In order to decide whether the speed distribution narrow or wide, consider $\sigma / < c >$. What is it?

2. Compute the number of collisions an argon atom has per second at 1 atm pressure and 25C. Assume that the argon atom has a 3Å diameter. What is the mean free path under these conditions?

3. At room temperature, two gases, ammonia and hydrochloric acid react to form a white solid, ammonium chloride; i.e.,

$$NH_3(g) + HCl(g) \to NH_4Cl(s).$$

Two balls, one soaked in concentrated HCl and the other in NH_4OH, are placed at the left and right ends of a 1m long evacuated glass tube, respectively. HCl and ammonia vaporize and travel down the tube, reacting to form a white ring where they meet. Where does the ring form?

4. (Silbey, Alberty & Bawendi, Problem 17.45) The vapor pressure of water at 25^oC is 3160 Pa. (a) If every water molecule that strikes the surface of liquid water sticks, what is the rate of evaporation of molecules from a square centimeter of surface? (b) Using this result, find the rate of evaporation in g/cm^2 of water into perfectly dry air.

5. The reaction

$$A + B \to AB$$

proceeds using a surface catalyst via the following mechanism:

$$A + S \xrightarrow{k_s} A^* + S$$

$$A^* + B \xrightarrow{k_{AB}} AB,$$

where A^* is a gas-phase intermediate and where the rate constants can be estimated using the collision theory developed in class.

a) Write down the kinetic equations for the overall rates of change of A, A^*, B, and AB (you should leave your answers in terms of k_s and k_{AB}).

b) It is often difficult to measure small concentrations of intermediates. Nonetheless, the fact that the concentration of A^* is very small can be used to simplify your answer in a). Make the so-called *steady-state approximation*, which, here, assumes that the net rate of change of the intermediate A^* is zero (usually the rate will be very small if the concentration of the intermediate is). This allows you to explicitly solve for $[A^*]$ and substitute your answer into the remaining kinetic equations. What do you get? How would you tell an experimentalist to plot their data in order to confirm your result? (HINT: remember how the integrated rate laws are tested).

6. An interference pattern is created using lasers in a gas of molecules that are photo-reactive. The lasers are adjusted to give an initial periodic concentration profile of the photo-reactive products of the form:

$$n(x, t = 0) \equiv n_0(1 + A \sin(kx)), \tag{1}$$

where k is the wavevector of the interference pattern and A is its amplitude. At t=0 the laser is switched off and the pattern starts to dissipate. Assume that Eq. (1) is valid for $t > 0$ (with a time dependent amplitude $A(t)$) and use the diffusion equation we derived in class to obtain an equation for $dA(t)/dt$. What is the solution to this equation and what does it predict for the 1/e-life of the pattern (i.e., where the amplitude falls to 1/e of its initial value)? Finally, evaluate your 1/e-lives for methane at 1 atm pressure and 298.15K, assuming that $k = 1.0$, 100.0, and 10^6 cm^{-1}. Use 0.4 nm for the diameter of methane.

18.3. Problem Set 3

DUE: Thursday, November 5, 2015

1. How much work will be produced in the isothermal, reversible expansion from $\bar{V}_1$ to $\bar{V}_2$ of a gas with the equation of state:

$$p\bar{V} = RT + \frac{(bRT - a)}{\bar{V}}$$

2. (Barrow, Problem 5-1) The acceleration due to gravity on the earth's surface is about 9.8 $m\ sec^{-2}$.

a) What is the force of gravity on a 1-kg mass?

b) How much mechanical energy could be obtained by fully harnessing the downward movement of a 1-kg mass through a distance of 58 m (the height of Niagara Falls)?

c) How much thermal energy would be produced if the mass were allowed to fall freely through this distance?

d) If the mass consisted of water and all the thermal energy were absorbed by the water, How much would the temperature of the water rise?

3. a) Consider a process where the heat absorbed by the system per mole is given by:*

$$đ\bar{Q} \equiv -\frac{3a}{4T^{3/2}\bar{V}}\,dT - \left(\frac{RT}{\bar{V}-b} + \frac{a}{2T^{1/2}\bar{V}^2}\right)d\bar{V}.$$

Evaluate the heat absorbed by the system along the following paths:

i) $T_1, \bar{V}_1 \rightarrow T_2, \bar{V}_1 \rightarrow T_2, \bar{V}_2$

ii) $T_1, \bar{V}_1 \rightarrow T_1, \bar{V}_2 \rightarrow T_2, \bar{V}_2$

b) Show that 1/T is an integrating factor for $đQ$ (i.e., $đQ/T$ becomes the differential of a state function) by evaluating the integral of $đQ/T$ along paths i) and ii).

4. An average man (mass = 70 kg, specific heat - same as water) produces about 10^4 kJ of heat each day through metabolic activity.

i) If he were an isolated system, what would his temperature rise be in one day?

ii) He is, of course, really an open system--losing heat through evaporation of water. How much water must he evaporate per day to maintain his constant temperature *of* 37^oC? You must first calculate ΔH_{vap} *at* 37^o.

Note that the notation is suggesive of the van der Walls equation. This cannot be the case. If you look at your result for the first part of path i), i.e., $T_1, V_1 \rightarrow T_2, V_1$, you'll see that $đ\bar{Q} < 0$ if $a > 0$ and $T_2 > T_1$; i.e., heat is released on raising the temperature at constant volume, thereby making $C_V < 0$. This is unphysical unless $a < 0$. Letting $a \rightarrow -a$ fixes this problem.

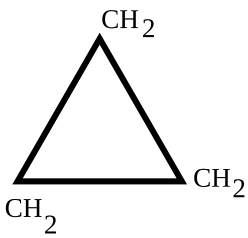
iii) The heat of combustion of cane sugar is 3.95 kcal/g. How many grams of sugar will furnish energy for one day's metabolism, assuming the transfer of heat from cane sugar bonds to metabolic heat to be perfectly efficient?

5. In the thermite reaction:

$$2Al_{(s)} + Fe_2 0_{3(s)} \rightarrow 2Fe(l) + Al_2 0_3(s),$$

what is the maximum temperature attainable by the products? This is known as the adiabatic flame temperature. Assume that the reactants are at 1 atm pressure and 25C, and that all heat capacities are constant over the required temperature ranges. You will need to go to tables of thermodynamic constants; a good place to look is in Lange's Hanbook of Chemistry or in the CRC handbook (both are available on-line at McGill). Is the assumption that $Al_2 0_3$ is solid in writing the reaction reasonable? Briefly describe how would you change your calculation if Al_2O_3 wasn't solid?

6. Consider the following two isomers of C_3H_6:



Cyclopropane

Propene

a) Calculate ΔH for the interconversion of cyclopropane and propene using a table of standard heats of formation.

b) Calculate ΔH for this reaction using a table of bond energies.

c) Which answer is more reliable? Why? What are the sources of error?

d) Which compound would yield more heat upon complete combustion in oxygen?

18.4. Problem Set 4

DUE: Thursday, November 19, 2015

1. (Castellan, Problem 7.30) The Joule-Thompson coefficient for a van der Waals gas is given by $\mu_{JT} = (2a/RT - b)/\bar{C}_P$. At 300K, calculate the value of ΔH for the isothermal, compression of 1 mole of nitrogen from 1 to 500 atm: $a = 0.136\ m^6\ Pa/mol^2$ and $b = 0.0391 dm^3/mol$.

2. (Castellan, Problem 7.31) The boiling point of nitrogen is -196C and $\bar{C}_P = 7/2\ R$. The van der Waals constants and μ_{JT} are given in the preceding problem. What must the initial pressure be if nitrogen, in a single stage Joule-Thompson expansion, is to drop in temperature from 25 C to the boiling point? (The final pressure is 1atm).

3. A chemistry 223 student was overheard arguing with a friend in management about why we have winter heating. The latter stated that it was to make the air in the room warmer, while the chemistry 223 student claimed that it was to increase the energy content of the air in the room. Who is right? Why?

4. (Castellan, Problem 8.4)

a) Liquid helium boils at about 4K and liquid hydrogen boils at about 20K. What is the efficiency of a reversible Carnot engine operating between heat reservoirs at these temperatures?

b) If we wanted the same efficiency as in part (a) for an engine with a cold reservoir at 300K, what must the temperature of the hot reservoir be?

5. (Castellan, Problem 8.17) Consider the following cycle using 1 mol of an ideal gas, initially at 20C and 1 atm pressure:

Step 1. Isothermal expansion against zero pressure to double the volume (Joule expansion).
Step 2. Isothermal, reversible compression from 1/2 atm to 1 atm.

a) Calculate the value of $\oint đ\, Q/T$.

b) Calculate ΔS for step 2.

c) Realizing that for the cycle, $\Delta S_{cycle} = 0$, find ΔS for step 1.

d) Show that ΔS for step 1 is *not* equal to the Q for step 1 divided by T. Why isn't it?

6. Consider a system comprised of two 1000g blocks of copper ($c_p = 0.1\ cal/g/^o$K). If one block is at 300K and the other is at 400K, what is the maximum amount of work that can be extracted from the system if no additional heat is allowed to flow into or out of the system. What will the final temperature be after the work is extracted? Describe a process whereby you could extract the maximum work. In working out this problem, ignore any PV work associated with the expansion of the blocks.

18.5. Problem Set 5

DUE: Tuesday, December 1, 2015

1. (Castellan, Problem 9.1) The temperature of 1 mole of an ideal gas is increased from 100K to 300K; $\bar{C}_V = \frac{3}{2} R$.

a) Calculate ΔS if the volume is constant.

b) Calculate ΔS if the pressure is constant.

c) What would ΔS be if 3 moles were used instead of 1 mole?

2. (Castellan, Problem 9.10) The standard entropy of lead at 25C is $\bar{S}^o_{298} = 64.80\ J/K\ mol$. The heat capacity of solid lead is: $\bar{C}_P(s)[J/K\ mol] = 22.13 + 0.01172T + 0.96 \times 10^5 T^{-2}$. The melting point is 327.4 C and the heat of fusion is $4770 J/mol$. The heat capacity of liquid lead is $\bar{C}_P(l)[J/K\ mol] = 32.51 - 0.00301T$.

a) Calculate the standard entropy of liquid lead at 500 C.

b) Calculate the ΔH for changing solid lead at 25C to liquid lead at 500C.

3. (Castellan, Problem 9.18) Consider one mole of an ideal gas, $\bar{C}_V = \frac{3}{2} R$, in the initial state: 300K, 1 atm. For each transformation, (a) through (g), calculate Q, W, ΔE, ΔH, and ΔS; compare ΔS to Q/T.

a) At constant volume, the gas is heated to 400K.

b) at constant pressure, 1 atm, the gas is heated to 400K.

c) The gas is expanded isothermally and reversibly until the pressure drops to 1/2 atm.

d) The gas is expanded isothermally against a constant external pressure equal to 1/2 atm until the gas pressure reaches 1/2 atm.

e) The gas is expanded isothermally against zero opposing pressure (Joule expansion) until the pressure of the gas is 1/2 atm.

f) The gas is expanded adiabatically against a constant pressure of 1/2 atm until the final pressure is 1/2 atm.

g) The gas is expanded adiabatically and reversibly until the final pressure is 1/2 atm.

4. (Castellan, Problem 9.26) Show that

$$\left(\frac{\partial \alpha}{\partial P}\right)_T = -\left(\frac{\partial \kappa}{\partial T}\right)_P,$$

where α and κ are the thermal expansion coefficient and isothermal compressibility, respectively.

5. (Castellan, Problem 10.23) From the purely mathematical properties of the exact differential

$$dE = C_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV,$$

show that if $\left(\partial E/\partial V\right)_T$ is a function only of volume, then C_V is a function only of temperature.

6. (Castellan, Problem 10.28) Knowing that $dS = \frac{C_P}{T} dT - V\alpha dP$, show that

a) $(\partial S/\partial P)_V = \kappa C_V/T\alpha$.

b) $(\partial S/\partial V)_P = C_P/TV\alpha$.

c) $\kappa_S \equiv -V^{-1}(\partial V/\partial P)_S = \kappa/\gamma$, where $\gamma \equiv C_P/C_V$, where κ_S is known as the adiabatic compressibility and governs the speed of sound in materials.

18.6. Problem Set 6

DUE: Tuesday, December 15, 2015

1. (Castellan, Problem 11.4)

a) Calculate the entropy of mixing of 3 moles of hydrogen with 1 mole of nitrogen.

b) Calculate the Gibbs free energy of mixing at 25C.

c) At 25C, calculate the Gibbs energy of mixing $(1-\xi)$ moles of nitrogen, $3(1-\xi)$ moles of hydrogen, and 2ξ moles of ammonia as a function of ξ. Plot your result for $0 \le \xi \le 1$.

d) If $\Delta G_f^o(NH_3) = -16.5 kJ/mol$ at 25C, calculate the Gibbs energy of the mixture for $0 \le \xi \le 1$. Plot G versus ξ if the initial state is the mixture of 1 mole of N_2 and 3 moles of H_2.

e) Calculate G for $\xi_{equilibrium}$ at $P = 1 atm$.

NOTE: Use a spreadsheet or other program to do the numerical work in this problem. Use 10 or so points for your plots.

2. (Castellan, Problem 11.8) At 500K we have the data

Substance	ΔH^o_{500} (kJ/mol)	S^o_{500} $(J/K\ mol)$
$HI(g)$	32.41	221.63
$H_2(g)$	5.88	145.64
$I_2(g)$	69.75	279.94

One mole of H_2 and one mole of I_2 are placed in a vessel at 500K. At this temperature only gases are present and the equilibrium

$$H_2(g) + I_2(g) \rightleftarrows 2HI(g)$$

is established. Calculate K_P at 500K and the mole fraction of HI present at 500K and 1atm. What happens at 10 atm?

3. (Castellan, Problem 11.10) For ozone at 25 C, $\Delta G_f^o(O_3) = 163.2\ kJ/mol$.

a) At 25C, compute the equilibrium constant, K_P for the reaction

$$3O_2(g) \rightleftarrows 2O_3(g)$$

b) By assuming that the advancement at equilibrium, ξ_{eq} is very much less than unity (why is this reasonable?), show that $\xi_{eq} \approx \frac{3}{2}\sqrt{PK_P}$. (Let the original number of moles of O_2 and O_3 be 3 and zero, respectively).

c) Calculate K_x and K_c at 5 atm.

4. (Castellan, Problem 11.22) Consider the equilibrium

$$CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g).$$

a) At 1000K the composition of a sample of the equilibrium mixture is:

Substance	CO_2	H_2	CO	H_2O
mol %	27.1	27.1	22.9	22.9

Calculate K_P and ΔG^o at 1000K.

b) Given the answer to part (a) and the data:

Substance	CO_2	H_2	CO	H_2O
ΔH_f^o (kJ/mol)	-393.51	0	-110.52	-241.81

Calculate ΔG^o for this reaction at 298.15K. Compare your answer to that computed directly at 25C. What are the sources of any discrepancy?

5. (Castellan, Problem 11.32) For the reaction

$$Hg(l) + \tfrac{1}{2}O_2(g) \rightleftarrows HgO(s),$$

$$\Delta G^o = -91044 + 1.54\,T \ln T + 103.81T - 10.33 \times 10^{-3} T^2 - \frac{0.42 \times 10^5}{T} \quad (J/mol).$$

a) What is the vapor pressure of oxygen over liquid mercury and solid HgO at 600K?

b) Express $\ln K_P$, ΔH^o, and ΔS^o as functions of temperature.

6. (Castellan, Problem 11.35) At 25C the data for the various isomers of C_5H_{10} in the gas phase are

Substance	ΔH_f^o (kJ/mol)	ΔG_f^o (kJ/mol)	$\log_{10} K_f$
A = 1-pentene	-20.920	78.605	-13.7704
B = cis-2-pentene	-28.075	71.852	-12.5874
C = trans-2-pentene	-31.757	69.350	-12.1495
D = 2-methyl-1-butene	-36.317	64.890	-11.3680
E = 3-methyl-1-butene	-28.953	74.785	-13.1017
F = 2-methyl-2-butene	-42.551	59.693	-10.4572
G = cyclopentane	-77.24	38.62	-6.7643

Consider the equilibria

$$A \rightleftarrows B \rightleftarrows C \rightleftarrows D \rightleftarrows E \rightleftarrows F \rightleftarrows G$$

which might be established with a suitable catalyst.

a) Calculate the mole ratios of A/G, B/G, ..., F/G present at equilibrium at 25C.

b) Do these ratios depend on the total pressure?

c) Calculate the mole percents of the various species in the equilibrium mixture.

d) Calculate the composition of the equilibrium mixture at 500K.

7. (Castellan, Problem 11.40) One mole of N_2O_4 is placed in a vessel. When the equilibrium

$$N_2O_4(g) \rightleftarrows 2NO_2(g)$$

is established, the enthalpy of the equilibrium mixture is

$$H = (1-\xi)\bar{H}^o(N_2O_4, g) + 2\xi\bar{H}^o(NO_2, g).$$

What assumption are we making by using molar enthalpies of pure substances here? If the mixture remains in equilibrium as the temperature is raised,

a) show that the heat capacity is given by

$$\frac{C_P}{R} = (1-\xi)\,\frac{\bar{C}_P(N_2O_4, g)}{R} + 2\xi\,\frac{\bar{C}_P(NO_2, g)}{R} + \tfrac{1}{2}\,\xi(1-\xi^2)\left(\frac{\Delta H^o}{RT}\right)^2;$$

b) Show that the last term has a maximum value when $\xi = 1/\sqrt{3}$;

c) Plot C_P/R versus T from 200K to 500K at 1 atm using $\bar{C}_P(N_2O_4, g)/R = 9.29$, $\bar{C}_P(NO_2, g)/R = 4.47$, $\Delta H^o_{298} = 57.20 kJ/mol$; and $\Delta G^o_{298} = 4.77 kJ/mol$.

8. (Castellan, Problem 11.43) An athlete in the weight room lifts a 50kg mass through a vertical distance of 2.0m ($g = 9.8 m/s^2$). The mass is allowed to fall through the 2.0m distance while coupled to an electrical generator. The electrical generator produces an equal amount of electrical work which is used to produce aluminium by the Hall electrolytic process

$$Al_2O_3(soln) + 3C(graphite) \rightarrow 2Al(l) + 3CO(g).$$

$\Delta G^o = 593\, kJ/mol$. How many times must the athlete lift the 50kg mass to proved sufficient Gibbs energy to produce one soft drink can ($\approx$ 27g). Note: This is the energy for the electrolysis and ignores the efficiency of the generator and other losses. The actual number is roughly three times larger than your number.

19. Past Midterm Exams

19.1. 2012 Midterm Exam

INSTRUCTIONS

1. No books or notes are permitted.
2. Calculators are not needed and are **not** permitted.
3. Answer all questions and show all work clearly.
4. There are 5 questions and each is of equal value.
5. Be sure to indicate the total number of exam books handed in on your exam book and on the log sheet.
6. You may need the following data:

Useful Constants

Constant	Value
Gas Constant, R	8.31442 $J\,K^{-1}\,mole^{-1}$
Boltzmann's Constant, k_B	$1.381 \times 10^{-23} J/K$
Speed of Light in Vacuum	$2.998 \times 10^{8} m/sec$
Faraday, F	96,484.6 Coul/mole
Standard Atmosphere	$1.01325 \times 10^{5} Pa$
Avogadro's Number	6.0225×10^{23}
1 cal	4.184 J

7. You may need the following results from calculus:

$$\int_{-\infty}^{\infty} e^{-ax^2/2} dx = \sqrt{2\pi/a}, \qquad \int_A^B x\, e^{-ax^2/2} dx = \frac{1}{a}\left(e^{-aA^2/2} - e^{-aB^2/2}\right),$$

$$\int_A^B x^3 e^{-ax^2/2} dx = \frac{(aA^2+2)e^{-aA^2/2} - (aB^2+2)e^{-aB^2/2}}{a^2},$$

$$\int_A^B \frac{dx}{x} = \ln(B/A), \qquad \int_A^B \frac{dx}{x^2} = \frac{1}{A} - \frac{1}{B},$$

$$\ln(1+x) \approx x, \text{ and } \frac{1}{1-x} \approx 1 + x + x^2 + \cdots \text{ for } |x| \ll 1.$$

Thursday, October 25, 2012

8. Good Luck.

1. (20%)

a) What is the van der Waals equation of state? What do the various modifications to the ideal gas equation account for, and why do they have the forms they do?

b) Sketch the pressure-volume phase diagram for high, low and critical temperatures for the van der Waals equation. Identify the critical point and label the various regimes.

c) Use your result in part a) to derive equation(s) for the critical point in the pressure-volume phase diagram. What is the physical significance of the critical point?

d) What is the law of corresponding states? Describe how you would use the equations you got in part c) to transform the van der Waals equation into a form that shows this (Don't bother solving the equations).

2. (20%) Starting from the Maxwell-Boltzmann velocity distribution, derive the rate law and expression for the rate constant for a catalytic surface reaction. Assume that the activation energy is E_A. What assumption(s) are you making?

3. (20%) Give definitions, or a general equation defining the quantity, for the following terms in thermodynamics:

a) Work. b) Path.
c) Enthalpy d) Reversible.
e) State Function.

4. (20%)

a) What are extensive and intensive quantities in thermodynamics? Give an example of each.

b) For an extensive function, $A(T, P, N_{1,} N_2, \ldots, N_r)$, derive Euler's theorem and show how partial molar quantities can be used to represent A. For concreteness, assume that T, P, and the N_i have their usual meanings; i.e., temperature, pressure, and number of moles of compound i, respectively.

c) Derive the Gibbs-Duhem relation related to your result in b).

d) The energy is an extensive quantity and can be considered to be a function of three extensive quantities (for a one component system); namely,

$$E = E(S, V, N),$$

where V is the system's volume, N is the number of moles, and S is the entropy of the system (to be covered in detail later in the course). For small reversible changes in state

$$dE = TdS - PdV + \mu dN,$$

where T, P and μ are the system's temperature, pressure and chemical potential, respectively (the chemical potential is intensive). Generalize your answer in part b) and show that

$$E = TS - PV + \mu N.$$

What is the Gibbs-Duhem relation in this case?

5. (20%) The reaction for nuclear fission is

$$n + {}^{235}U \xrightarrow{k_1} X + Y + \alpha n, \tag{1}$$

where n is a neutron, X and Y are the fission products, and α is the number of neutrons released, usually between 2 and 3. This is an example of what is known as a branching chain reaction and can lead to runaway or explosive kinetics. Very crudely, this is prevented by introducing a so-called moderator, e.g., graphite or D_2O, that slows the neutrons down and a neutron absorber, A, e.g., ${}^{238}U$ or the so-called control rods, into the reactor, or by having the neutron escape. These last two processes are approximately described by the following elementary reactions:

$$n + A \xrightarrow{k_2} \text{stable products}, \qquad \text{and} \qquad n \xrightarrow{k_3} \text{escapes the system}, \tag{2}$$

respectively.

a) Derive the rate equation governing the neutron concentration, $[n](t)$.

b) Under the assumption that everything but the neutrons is in large excess (this is valid at least initially):

   i) What order kinetics does your answer in part a) become?

   ii) What is the integrated rate law for the neutrons?

   iii) How should you plot experimental data to prove the mechanism?

c) What are the conditions for a stable or run-away/explosive reactions?

19.2. 2013 Midterm Exam.

INSTRUCTIONS

1. **No** books or notes are permitted.
2. Calculators are **not** needed and are **not** permitted.
3. Answer all questions and show all work clearly.
4. There are 5 questions and the exam has 3 pages including this one.
5. Be sure to indicate the total number of exam books handed in on your exam book and on the log sheet.
6. You may need the following data:

Useful Constants

Constant	Value
Gas Constant, R	8.31442 $J\ K^{-1}\ mole^{-1}$
Boltzmann's Constant, k_B	$1.381 \times 10^{-23} J/K$
Speed of Light in Vacuum	$2.998 \times 10^{8} m/sec$
Faraday, F	96,484.6 Coul/mole
Standard Atmosphere	$1.01325 \times 10^{5} Pa$
Avogadro's Number	6.0225×10^{23}
1 cal	4.184 J

7. You may need the following results from calculus:

$$\int_{-\infty}^{\infty} e^{-ax^2/2} dx = \sqrt{2\pi/a}, \qquad \int_A^B x\, e^{-ax^2/2} dx = \frac{1}{a}\left(e^{-aA^2/2} - e^{-aB^2/2}\right),$$

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2/2} dx = \frac{\sqrt{2\pi/a}}{a}, \qquad \int_A^B x^3 e^{-ax^2/2} dx = \frac{(aA^2+2)e^{-aA^2/2} - (aB^2+2)e^{-aB^2/2}}{a^2},$$

$$\int_A^B \frac{dx}{x} = \ln(B/A), \qquad \int_A^B \frac{dx}{x^2} = \frac{1}{A} - \frac{1}{B},$$

$$\ln(1+x) \approx x, \text{ and } \frac{1}{1-x} \approx 1 + x + x^2 + \cdots \text{ for } |x| \ll 1.$$

8. Good Luck.

1. (20%) Give a definition or an equation defining the following properties:

a) Mean free path
b) The enthalpy
c) Detailed balance
d) Steady state approximation
e) The First Law of Thermodynamics
f) A reversible process
g) Work in thermodynamics
h) State function
i) The effusion rate
j) The speed probability density.

2. (20%) Consider the homogeneous gas phase elementary reaction

$$2A(g) \stackrel{k_1}{\rightarrow} Products.$$

Use the kinetic theory of gases to derive a *realistic* form for the rate law, and the corresponding expression for the rate coefficient, k_1. Be careful to define the symbols you use and clearly state any assumptions you make.

3. (20%)

a) You suspect that a chemical reaction obeys second order kinetics; how you would plot your experimental data to prove or disprove the assumed mechanism? Show why and show your work!

b) Consider the following mechanism[1], for the decomposition of ozone:

$$O_3(g) + M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O_2(g) + O(g) + M \tag{3.1}$$

and

$$O(g) + O_3(g) \stackrel{k_2}{\rightarrow} 2O_2(g), \tag{3.2}$$

where M is an inhomogeneous catalyst (e.g., walls or particulate matter in the system).

i) Write down the kinetic equations governing the reaction rates of O_3, O_2 and O.

ii) Use the steady-state approximation to simplify your result; in particular, what is the resulting kinetic equation for the rate of O_3 consumption?

[1] S.W. Benson and A.E. Axworthy, J. Chem. Phys, **26**, 1718 (1957).

iii) How does your answer in part ii) simplify if the O_3 concentration is either high or low? (Be more specific about what you mean by "high" or "low").

iv) To what order reaction, if any, do your answers in part iii) correspond?

4. (15%, FROM THE HOMEWORK) An interference pattern is created using lasers in a gas of molecules that are photo-reactive (irreversibly). The lasers are adjusted to give an initial periodic concentration profile of the photo-reactive products of the form:

$$n(x, t = 0) \equiv n_0(1 + A\sin(kx)), \tag{4.1}$$

where $n(x, t)$ is the density of the photo-reactive species, k is the wave-vector of the interference pattern and A is its amplitude. At t=0 the laser is switched off and the pattern starts to dissipate. Assume that Eq. (4.1) is valid for $t > 0$, with a time dependent amplitude $A(t)$, and use the diffusion equation we derived in class to obtain an equation for $dA(t)/dt$. What is the solution to this equation and what does it predict for the 1/e-life of the pattern (i.e., where the amplitude falls to 1/e of its initial value)?

5. (25%)

a) Explain how the heat capacities, C_P and C_V, are related to the energy and enthalpy.

b) Show that

$$C_P - C_V = \alpha V\left[P + \left(\frac{\partial E}{\partial V}\right)_{T,N}\right], \tag{5.1}$$

where $\alpha \equiv V^{-1}(\partial V/\partial T)_{P,N}$ is the thermal expansion coefficient.

c) Describe the Joule-Thompson experiment. What thermodynamic quantity is constant in the experiment?

d) Define the Joule-Thompson coefficient, μ_{JT}, and show, in part, using Eq. (5.1), that

$$\mu_{JT} = -\frac{V}{C_P}\left[1 - \frac{\kappa}{\alpha V}(C_P - C_V)\right], \tag{5.2}$$

where $\kappa \equiv -V^{-1}(\partial V/\partial P)_{T,N}$ is the isothermal compressibility.

19.3. 2014 Midterm Exam

INSTRUCTIONS

1. **No** books or notes are permitted.
2. Calculators are **not** needed and are **not** permitted.
3. Answer all questions and show all work clearly.
4. There are 5 questions and the exam has 3 pages including this one.
5. Be sure to indicate the total number of exam books handed in on your exam book and on the log sheet.
6. You may need the following data:

Useful Constants

Constant	Value
Gas Constant, R	$8.31442\ J\ K^{-1}\ mole^{-1}$
Boltzmann's Constant, k_B	$1.381 \times 10^{-23} J/K$
Speed of Light in Vacuum	$2.998 \times 10^{8} m/sec$
Faraday, F	96,484.6 Coul/mole
Standard Atmosphere	$1.01325 \times 10^{5} Pa$
Avogadro's Number	6.0225×10^{23}
1 cal	4.184 J

7. You may need the following results from calculus:

$$\int_{-\infty}^{\infty} e^{-ax^2/2} dx = \sqrt{2\pi/a}, \qquad \int_A^B x\, e^{-ax^2/2} dx = \frac{1}{a}\left(e^{-aA^2/2} - e^{-aB^2/2}\right),$$

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2/2} dx = \frac{\sqrt{2\pi/a}}{a}, \qquad \int_A^B x^3 e^{-ax^2/2} dx = \frac{(aA^2+2)e^{-aA^2/2} - (aB^2+2)e^{-aB^2/2}}{a^2},$$

$$\int_A^B \frac{dx}{x} = \ln(B/A), \qquad \int_A^B \frac{dx}{x^2} = \frac{1}{A} - \frac{1}{B},$$

$$\ln(1+x) \approx x, \text{ and } \frac{1}{1-x} \approx 1 + x + x^2 + \cdots \text{ for } |x| \ll 1.$$

Tuesday, October 21, 2014

8. Good Luck.

1. (20%) Define or give an equation defining the following terms:

a) Extensive.

b) Partial molar quantity.

c) State function.

d) A reversible change.

e) The mean free path in a one-component gas.

2. (20%) (From Silbey, Alberty and Bawendi, *Physical Chemistry*) In the mid-1970's it was discovered that chlorine atoms from the photolysis of chlorofluorohydrocarbons (e.g. $CFCl_3 + h\nu \to CFCl_2 + Cl$, etc.) at the level of the ozone layer can catalyze the decomposition of ozone through the following mechanism*.

$$Cl + O_3 \xrightarrow{k_1} ClO + O_2 \tag{1a}$$

and

$$ClO + O \xrightarrow{k_2} Cl + O_2. \tag{1b}$$

a) What is the overall reaction for this mechanism?

b) Write out the kinetic equations for each of the species involved in this mechanism. In particular, what does your mechanism say for the rate of change of $[Cl] + [ClO]$?

c) What is/are the intermediate(s) for this reaction?

d) Invoke the steady-state approximation and write out the overall rate law. [Hint: you may have to use your result in the last part of b)].

e) Briefly discuss your result, and in particular, comment on any limiting cases where simple n^{th} order kinetics is obtained.

---

*The destruction of ozone by chlorine atoms in the stratosphere has become a serious issue because of the "ozone hole" in the Antarctic region, which can be surveyed by satellite. This has led to international controls on the manufacture of $CFCl_3$ and CF_2Cl_2. Several cycles of the type given in Eq. (1) are involved and there has been intense interest in quantitative calculations of the lifetimes of various chlorofluorohydrocharbons in the stratosphere. The 1995 Nobel Prize in chemistry was awarded to Paul Crutzen, Mario J. Molina, and F. Sherwood Rownald for their research on this topic.

3. (20%, From the homework) At room temperature, two gases, ammonia and hydrochloric acid react to form a white solid, ammonium chloride; i.e.,

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s).$$

Two balls, one soaked in concentrated HCl and the other in NH_4OH, are placed at the left and right ends of a 1m long evacuated glass tube, respectively. HCl and ammonia vaporize and travel down the tube, reacting to form a white ring where they meet. Where does the ring form?

4. (20%) Derive expressions for the following (be sure to define all symbols and explain any assumptions you make):

a) $Z_{A\ with\ B}$ the number of collisions per unit time an A molecule collides with a B in an dilute gas.

b) The effusion rate.

c) The reaction rate constant for the gas phase reaction:

$$A + A \rightarrow Products$$

d) The van der Waals equation of state. In particular, explain the physical motivations behind any of modifications you introduce and justify the mathematical forms they have.

5. (20%) State the first law of thermodynamics, carefully defining the symbols you use. Briefly discuss its significance. Under what conditions does it simplify, in particular, leading to something that can readily measured.

19.4. 2015 Midterm Exam

INSTRUCTIONS

1. **No** books or notes are permitted.
2. Calculators are permitted.
3. Answer all questions and show all work clearly.
4. There are 5 questions and the exam has 2 pages including this one.
5. Be sure to indicate the total number of exam books you hand in on your exam book and on the log sheet.
6. You may need the following data:

Useful Constants

Constant	Value
Gas Constant, R	8.31442 $J\ K^{-1}\ mole^{-1}$
Boltzmann's Constant, k_B	$1.381 \times 10^{-23} J/K$
Speed of Light in Vacuum	$2.998 \times 10^{8} m/sec$
Faraday, F	96,484.6 Coul/mole
Standard Atmosphere	$1.01325 \times 10^{5} Pa$
Avogadro's Number	6.0225×10^{23}
1 cal	4.184 J

7. You may need the following results from calculus:

$$\int_{-\infty}^{\infty} e^{-ax^2/2} dx = \sqrt{2\pi/a}, \qquad \int_A^B x\, e^{-ax^2/2} dx = \frac{1}{a}\left(e^{-aA^2/2} - e^{-aB^2/2}\right),$$

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2/2} dx = \frac{\sqrt{2\pi/a}}{a}, \qquad \int_A^B x^3 e^{-ax^2/2} dx = \frac{(aA^2+2)e^{-aA^2/2} - (aB^2+2)e^{-aB^2/2}}{a^2},$$

$$\int_A^B \frac{dx}{x} = \ln(B/A), \qquad \int_A^B \frac{dx}{x^2} = \frac{1}{A} - \frac{1}{B},$$

$$\ln(1+x) \approx x, \text{ and } \frac{1}{1-x} \approx 1 + x + x^2 + \cdots \text{ for } |x| \ll 1.$$

8. Good Luck.

1. (20%) For each of the following quantities, give a defining equation and briefly discuss their physical meaning:

a) The isothermal compressibility. b) The critical point.
c) The law of corresponding states. d) The diffusion flux.
e) Detailed balance.

2. (20%) Starting from the Maxwell-Boltzmann velocity distribution, derive an expression for the average number of reactive collisions on a surface per unit area per unit time. Assume that the normal component of velocity must exceed some threshold velocity for reaction to occur.

3. (20%, Castellan, Problem 32.37) A mechanism proposed for the gas phase decomposition of N_2O_5 is

$$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} NO_2 + NO_3 \overset{k_2}{\rightarrow} NO + O_2 + NO_2 \tag{3.1}$$

and

$$NO + NO_3 \overset{k_3}{\rightarrow} 2NO_2. \tag{3.2}$$

a) Write out kinetic equations for each of the species involved in this mechanism.

b) Invoke the steady-state approximation for NO_3 and NO and derive the rate of disappearance of N_2O_5.

c) Briefly discuss your result; in particular, comment on any limiting cases where simple n^{th} order kinetics is obtained.

4. (20%, From the homework, Silbey, Alberty & Bawendi, Problem 17.45) The vapor pressure of water at 25^oC is 3160 Pa. (a) If every water molecule that strikes the surface of liquid water sticks, what is the rate of evaporation of molecules from a square centimeter of surface? (b) Using this result, find the rate of evaporation in $g\ cm^{-2}\ s^{-1}$ of water into perfectly dry air.

5. (20%)

a) Write down the van der Waals equation of state and briefly explain the physical origin of the various modifications to the ideal gas law.

b) Show how the van der Walls equation leads to the appearance of a critical point. Derive the equations giving the critical point (*you don't need to solve them*).

c) Show how to turn the van der Waals equation into virial expansion; in particular, what is the second virial coefficient?

20. Past Final Exams

20.1. 2012 Final Exam

INSTRUCTIONS

1. No books or notes are permitted. Translation dictionaries and calculators are permitted.
2. Answer all questions in the exam book and show all work clearly.
3. There are 3 pages (including this one) and 5 questions, each of equal value.
4. Be sure to indicate the total number of exam books handed in on book 1.
5. **Keep the exam.**
6.

Useful Constants

Constant	Value
Gas Constant, R	8.31442 $J\ K^{-1}\ mol^{-1}$
Boltzmann's Constant, k_B	$1.381 \times 10^{-23} J/K$
Standard Atmosphere	$1.01325 \times 10^{5} Pa$
Avogadro's Number	6.0225×10^{23}
1 cal	4.184 J

7. You may need the following results from calculus:

$$\int_{-\infty}^{\infty} e^{-ax^2/2} dx = \sqrt{2\pi/a}, \qquad \int_A^B x\, e^{-ax^2/2} dx = \frac{1}{a}\left(e^{-aA^2/2} - e^{-aB^2/2}\right),$$

$$\int_A^B x^3 e^{-ax^2/2} dx = \frac{(aA^2+2)e^{-aA^2/2} - (aB^2+2)e^{-aB^2/2}}{a^2},$$

$$\int_A^B \frac{dx}{x} = \ln(B/A), \qquad \int_A^B \frac{dx}{x^2} = \frac{1}{A} - \frac{1}{B},$$

$$\ln(1+x) \approx x, \text{ and } \frac{1}{1-x} \approx 1 + x + x^2 + \cdots \text{ for } |x| \ll 1.$$

8. Good Luck.

Monday, December 17, 2012

1. (20%, Castellan, Problem 32.36) Consider the following mechanism for the decomposition of ozone into oxygen:

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O_2 + O \tag{1}$$

and

$$O_3 + O \overset{k_2}{\rightarrow} 2O_2. \tag{2}$$

a) Derive the rate expressions for each species involved in the reaction.

b) What species is the most likely to be an intermediate? What happens to your expression for dO_3/dt in this case?

c) Under what condition will the reaction be first order in ozone? Show how the equation for dO_3/dt reduces in this situation.

2. (20%) For each of the following give a definition (an equation is sufficient as long as you define your terms):

a) A Maxwell relation.
b) The Clausius Inequality.
c) The third Law of Thermodynamics.
d) Maximum work obtainable from a constant T,N process.
e) The chemical potential of one of the components in an ideal gas mixture.

3. (20%)

a) What is the Joule-Thompson expansion?

b) Show what remains constant during the Joule-Thompson expansion.

c) Define the Joule-Thompson coefficient, μ_{JT}.

d) Show that

$$\mu_{JT} = -\frac{V}{C_P}(1 - \alpha T),$$

where $\alpha \equiv V^{-1}(\partial V/\partial T)_{P,N}$ is the thermal expansion coefficient. (*Note*: you don't have to use the derivation we initially discussed in class).

4. (20%)

a) Derive the general expression governing where a chemical reaction comes to equilibrium; use the convention that the stochiometric coefficients are ν_i, with $\nu_i < 0$ for reactants and > 0 for products. Do not assume ideality (see the next part).

b) Show how your general expression in part a) simplifies for chemical reactions in ideal gas mixtures.

c) What is K_P and how is it used to determine the composition at equilibibium in an ideal gas mixture?

d) Use your expression in part c) to derive the Gibbs-Helmholtz equation.

5. (From the homework, 20%, Castellan, Problem 11.8) At 500K and 1 atm we have the data:

Substance	ΔH^o_{500} (kJ/mol)	S^o_{500} $(J/K\ mol)$
$HI(g)$	32.41	221.63
$H_2(g)$	5.88	145.64
$I_2(g)$	69.75	279.94

One mole of H_2 and one mole of I_2 are placed in a vessel at 500K. At this temperature only gases are present and the equilibrium

$$H_2(g) + I_2(g) \rightleftarrows 2HI(g)$$

is established. Calculate K_P at 500K and the mole fraction of HI present at 500K and 1 atm; show your work. What happens at 10 atm?

20.2. 2013 Final Exam

INSTRUCTIONS

1. No books or notes are permitted. Translation dictionaries and calculators are permitted.
2. Answer all questions in the exam book and show all work clearly.
3. There are 3 pages (including this one) and 5 questions, each of equal value.
4. Be sure to indicate the total number of exam books handed in on book 1.
5. **Keep the exam.**
6.

Useful Constants

Constant	Value
Gas Constant, R	$8.31442\ J\ K^{-1}\ mol^{-1}$
Boltzmann's Constant, k_B	$1.381 \times 10^{-23} J/K$
Standard Atmosphere	$1.01325 \times 10^5 Pa$
Avogadro's Number	6.0225×10^{23}
1 cal	4.184 J

7. You may need the following results from calculus:

$$\int_{-\infty}^{\infty} e^{-ax^2/2} dx = \sqrt{2\pi/a}, \qquad \int_A^B x\, e^{-ax^2/2} dx = \frac{1}{a}\left(e^{-aA^2/2} - e^{-aB^2/2}\right),$$

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2/2} dx = \frac{\sqrt{2\pi/a}}{a}, \qquad \int_A^B x^3 e^{-ax^2/2} dx = \frac{(aA^2+2)e^{-aA^2/2} - (aB^2+2)e^{-aB^2/2}}{a^2},$$

$$\int_A^B \frac{dx}{x} = \ln(B/A), \qquad \int_A^B \frac{dx}{x^2} = \frac{1}{A} - \frac{1}{B},$$

$$\ln(1+x) \approx x, \text{ and } \frac{1}{1-x} \approx 1 + x + x^2 + \cdots \text{ for } |x| \ll 1.$$

8. Good Luck.

1. (20%) One of the problems with solar energy systems is the need to store the solar energy for use at night or on cloudy days. One suggestion is to use the solar energy to dehydrate a hydrate and then rehydrate the material as needed. For example, consider

$$CuSO_4 \cdot 5H_2O(s) \;\rightarrow\; CuSO_4(s) + 5H_2O(g) \tag{1.1}$$

and

$$CuSO_4(s) + 5H_2O(l) \;\overset{25C}{\rightarrow}\; CuSO_4 \cdot 5H_2O(s). \tag{1.2}$$

Given the data in the table,

Table 1: Some Thermochemical Data at 25C[1]

Compound	ΔH_f^0 (kcal/mol)	ΔG_f^0 (kcal/mol)	S^0 (cal/K mol)
$CuSO_4(s)$	-184.00	-158.2	27.1
$CuSO_4 \cdot 5H_2O(s)$	-544.45	-449.3	73.0
$H_2O(l)$	-68.32	-56.69	16.72
$H_2O(g)$	-57.80	-54.64	45.11

[1]From Lange's Handbook of Chemistry, 10th edition.

a) Compute ΔH_{rxn}, ΔG_{rxn}, and ΔS_{rxn} at 25C for each reaction.

b) How much solar energy is required to dehydrate the copper sulphate?

c) How much heat is released upon rehydration?

d) At what (if any) temperature does the dehydration step become spontaneous? How much heat is required? What assumptions are you making?

2. (20%) Consider the Langmuir model for surface adsorption kinetics:

$$A + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AS, \tag{2.1}$$

where A is a gas-phase adsorbate and S is the surface. Langmuir assumed that the surface has N binding sites per unit area, and that adsorption was complete when all the binding sites are bound. In addition he assumed that the gas is in large excess (i.e., the bulk gas concentration is negligibly changed by the adsorption process, even with 100% coverage). Introduce the fractional surface covered, $\theta(t)$, as

$$[AS] \equiv N\theta(t) \;\text{ and }\; [S] \equiv N[1 - \theta(t)] \tag{2.2}$$

and:

a) Write down the kinetic equation for the fractional coverage. Express your answer in terms of the adsorbate's partial pressure in the gas phase.

b) What does your answer in a) predict for the pressure dependence of the fractional coverage at equilibrium? Sketch your result. (This is known as the Langmuir adsorption isotherm).

c) Assuming that $\theta(0) = 0$, solve the kinetic equations to give the time dependence of the adsorption.

d) How would you plot your data to demonstrate the validity of the mechanism?

3. (20%) Give the Clausius and Kelvin (Thompson) statements of the Second Law of Thermodynamics. Show that if the Clausius statement is correct then the Kelvin statement must also be.

4. (20%)

a) Give mathematical definitions for the following thermodynamic quantities, give their differential forms and natural variables, and state whether the quantity is a minimum or maximum at equilibrium under certain conditions (specify them):

i) Energy ii) Enthalpy
iii) Entropy iv) Helmholtz Free Energy
v) Gibbs Free Energy

b) Use Maxwell relations to express $C_P - C_V$ in terms of α, κ, T, and V.

c) Derive LeChatellier's principle.

5. (20% From the Homework: Castellan, Problem 11.32) For the reaction

$$Hg(l) + \tfrac{1}{2} O_2(g) \rightleftarrows HgO(s),$$

$$\Delta G^o_{rxn} = -91044 + 1.54\, T \ln T + 103.81T - 10.33 \times 10^{-3} T^2 - \frac{0.42 \times 10^5}{T} \quad (J/mol),$$

where T is the absolute temperature.

a) What is the vapor pressure of oxygen over liquid mercury and solid HgO at 600K?

b) Express $\ln K_P$, ΔH^o_{rxn}, and ΔS^o_{rxn} as functions of temperature.

20.3. 2014 Final Exam

INSTRUCTIONS

1. No books or notes are permitted. Translation dictionaries and calculators are permitted.
2. Answer all questions in the exam book and show all work clearly.
3. There are 3 pages (including this one) and 5 questions, each is of equal value. **NOTE THAT THE EXAM IS PRINTED ON BOTH SIDES OF THE PAPER**.
4. Be sure to indicate the total number of exam books handed in on book 1.
5. **Keep the exam.**
6.

Useful Constants

Constant	Value
Gas Constant, R	8.31442 $J\ K^{-1}\ mol^{-1}$
Boltzmann's Constant, k_B	$1.381 \times 10^{-23} J/K$
Standard Atmosphere	$1.01325 \times 10^{5} Pa$
Avogadro's Number	6.0225×10^{23}
1 cal	4.184 J

7. You may need the following results from calculus:

$$\int_{-\infty}^{\infty} e^{-ax^2/2} dx = \sqrt{2\pi/a}, \qquad \int_A^B x\, e^{-ax^2/2} dx = \frac{1}{a}\left(e^{-aA^2/2} - e^{-aB^2/2}\right),$$

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2/2} dx = \frac{\sqrt{2\pi/a}}{a}, \qquad \int_A^B x^3 e^{-ax^2/2} dx = \frac{(aA^2+2)e^{-aA^2/2} - (aB^2+2)e^{-aB^2/2}}{a^2},$$

$$\int_A^B \frac{dx}{x} = \ln(B/A), \qquad \int_A^B \frac{dx}{x^2} = \frac{1}{A} - \frac{1}{B}.$$

8. Good Luck.

Monday, December 15, 2014

1. (20%) Consider the following mechanism for a gas-phase reaction:

$$AY \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A + Y \quad \text{and} \quad A + X \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} AX. \tag{1.1}$$

a) What is the overall reaction and what is the intermediate?

b) Write out kinetic equations for the concentrations of each species.

c) Show that the mechanism conserves total A, X and Y (*HINT*: think of each of these as an individual atom).

d) Invoke the steady-state approximation and use it to eliminate the intermediate's concentration from the remaining kinetic equations.

e) Comment on the order of the resulting rate expressions in various limits.

2. (20%)

a) Sketch the pressure-volume diagram for a reversible Carnot cycle in an ideal gas. Be sure to label the conditions for the sub-paths of the process.

b) Calculate the amounts of heat and work absorbed by the system in each part of the cycle.

c) Use your results in part b) to find the engine efficiency for the cycle.

d) Use the Kelvin formulation of the Second Law of Thermodynamics and your result in part c) to obtain the Clausius inequality.

e) How does your result in part d) lead to the definition of the entropy?

3. (20%)

a) In general, show that

$$dS = \frac{C_V}{T}\, dT + \frac{\alpha}{\kappa}\, dV + \sum_i \left(\bar{S}_i - \frac{\alpha \bar{V}_i}{\kappa} \right) dN_i, \tag{3.1}$$

where $\alpha \equiv V^{-1}(\partial V/\partial T)_{P,N}$ and $\kappa \equiv -V^{-1}(\partial V/\partial P)_{T,N}$, are the thermal expansion coefficient and isothermal compressibility, respectively, while $\bar{S}_i$ and $\bar{V}_i$ are the partial molar entropy and volume, respectively.

b) Show that

$$C_P - C_V = \frac{VT\alpha^2}{\kappa}, \tag{3.2}$$

HINT: Where possible, use the much simpler, and shorter, derivations based on the techniques we developed later on in the course.

4. (20%)

a) How does the chemical potential in a one component ideal gas depend on pressure? Why?

b) Use your result in part a) to deduce the forms of the chemical potentials in an ideal gas mixture.

c) What governs the point at which a chemical reaction comes to equilibrium in a system with constant T, P, and N? Why?

d) By using your results in parts a)--c), show how the standard equilibrium constant formulation of chemical equilibrium in gases can be obtained. What is K_P, the constant pressure equilibrium constant.

e) Derive the Gibbs-Helmholtz equation governing the temperature dependence of the equilibrium constant.

5. (20%) Silbey, Alberty and Bawendi, Problem 5.64) Consider the reaction

$$2NOCl(g) \rightleftarrows 2NO(g) + Cl_2(g)$$

at 1 atm total pressure and $227C$. The partial pressure of the nitrosyl chloride ($NOCl$) is 0.64 atm and only $NOCl$ was present initially.

a) Calculate $\Delta\bar{G}^{(0)}_{rxn}$ for this reaction.

b) At what total pressure will the partial pressure of Cl_2 be 0.1 atm?

20.4. 2015 Final Exam

INSTRUCTIONS

1. No books or notes are permitted. Translation dictionaries and calculators are permitted.
2. Answer all questions in the exam book and show all work clearly.
3. There are 3 pages (including this one) and 5 questions, each is of equal value.
4. Be sure to indicate the total number of exam books handed in on book 1.
5. If you want me to grade material on the left hand page, indicate so explicitly.
6. Do not write in red.
7. **Keep the exam.**
8.

Useful Constants

Constant	Value
Gas Constant, R	$8.31442\ J\ K^{-1}\ mol^{-1}$
Boltzmann's Constant, k_B	$1.381 \times 10^{-23} J/K$
Standard Atmosphere	$1.01325 \times 10^{5} Pa$
Avogadro's Number	6.0225×10^{23}
1 cal	4.184 J

9. You may need the following results from calculus:

$$\int_{-\infty}^{\infty} e^{-ax^2/2} dx = \sqrt{2\pi/a}, \qquad \int_A^B x\, e^{-ax^2/2} dx = \frac{1}{a}\left(e^{-aA^2/2} - e^{-aB^2/2}\right),$$

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2/2} dx = \frac{\sqrt{2\pi/a}}{a}, \qquad \int_A^B x^3 e^{-ax^2/2} dx = \frac{(aA^2+2)e^{-aA^2/2} - (aB^2+2)e^{-aB^2/2}}{a^2},$$

$$\int_A^B \frac{dx}{x} = \ln(B/A), \qquad \int_A^B \frac{dx}{x^2} = \frac{1}{A} - \frac{1}{B}.$$

10. Good Luck.

1. (20%) For the reaction

$$A \rightarrow Products, \tag{20.4.1.1}$$

Lindemann showed how first order kinetics can arise homogeneously, without having to involve surfaces and/or externally applied radiation.

a) What is the Lindemann mechanism?

b) Apply the steady state approximation and use the result to derive the rates of product formation and A disappearance.

c) In general, what, if any, is the order of the reaction?

d) In what limits are first or second order kinetics obtained?

e) How else might homogeneous first order kinetics be obtained?

2. (20%)

a) Describe the Joule-Thompson expansion and show what state function remains constant during the experiment.

b) Define the Joule-Thompson coefficient, μ_{JT}.

c) Show that

$$\mu_{JT} = -\frac{V}{C_P}(1 - \alpha T), \tag{20.4.2.1}$$

where α is the thermal expansion coefficient.

d) What is μ_{JT} for an ideal gas?

3. (20%)

a) For an ideal gas how much work and heat are absorbed by the system, as well as ΔE, if

i) The gas is expanded reversibly and isothermally from (T_H, V_1) to (T_H, V_2').

ii) The gas is expanded reversibly and adiabatically from (T_H, V_2') to $(T_{C,} V_2)$. Dearive an expression showing how V_2' and V_2 related to T_H and T_C?

b) Sketch the reversible Carnot cycle and use your results in part a) to show that

$$\frac{Q_H}{T_H} + \frac{Q_c}{T_C} = 0. \tag{20.4.3.1}$$

c) What is the engine efficiency, η, of the reversible Carnot Engine?

d)
i) What is the Clausius statement of the Second Law of Thermodynamics?

ii) Use the Clausius statement to show that the efficiencies of all reversible Carnot engines are the same.

4. (20%, FROM THE HOMEWORK) Consider a system comprised of two 1000g blocks of copper ($c_p = 0.1\ cal/g/^oK$). If one block is at 300K and the other is at 500K, what is the maximum amount of work that can be extracted from the system if no additional heat is allowed to flow into or out of the system. What will the final temperature be after the work is extracted? Describe a process whereby you could extract the maximum work. In working out this problem, ignore any PV work associated with the expansion of the blocks.

5. (20%)

a) For the Helmholtz (A) and Gibbs (G) Free energies

i) Give their definitions and show what their differentials are.

ii) Under what conditions does each determine stable equilibrium? How?

iii) In what sense are ΔA or ΔG related to the possible work obtainable in some process?

b) Suppose we have a chemical reaction

$$\sum_i \nu_i A_i = 0, \tag{20.4.5.1}$$

under constant mass, temperature and *volume* conditions.

i) Work out what the general equilibrium condition.

ii) What does it become if all reactants and products are ideal gases?

iii) Consider the reaction

$$N_2O_4(g) \rightleftarrows 2NO_2(g). \tag{20.4.5.2}$$

Assuming that there were N_0 moles of N_2O_4 initially and no NO_2, what fraction of N_2O_4 has dissociated at equilibrium under constant volume conditions?

20.2. 2013 Final Exam 137
20.3. 2014 Final Exam 140
20.4. 2015 Final Exam 143