Chem 322, Physical Chemistry II: Lecture notes

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Preface

What is the first law of thermodynamics?
You do not talk about thermodynamics
What is the second law of thermodynamics?
You do not talk about thermodynamics

Chapter 2

Revision history

2/05: Original build
11/07: Corrected all typos caught to date and added some more material
1/08: Added more stuff and demos. Made the equilibrium section more pedagogical.
5/08: Caught more typos and made appropriate fixes to some nomenclature mistakes.
12/11: Started the next round of text changes and error corrections since I'm teaching this class again in spring 2012. Woah! I caught a whole bunch of problems that were present in the last version. It makes you wonder what I was thinking. Anyway, hindsight is 20/20.
12/12: Made next round of error corrections as caught by students during the spring semester of 2012. Made some other minor text changes and corrections. Also changed one derivation for the boiling point elevation in the colligative properties section.

Chapter 3

Introduction

This is left here for posterity (outdated)

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Class requirements

roughly 10 problem sets 3 exams and 1 final

Proposed grading scheme

Problem sets 10%
Exams 20%
Final 30%

Foreword to the student

To quote Gilbert Castellan from his well known textbook "Physical chemistry":

"On most campuses, the course in physical chemistry has a reputation for difficulty. It is not, nor should it be, the easiest course available; but to keep the matter in perspective, it must be said that the IQ of a genius is not necessary for understanding the subject... Finally, don't be put off by the reputation for difficulty. Many students have enjoyed learning physical chemistry." (this guy must have a sense of humor)

Now this is me speaking:
Unfortunately, this is an old, yet important, field. There have been many many people who have contributed things in this area over literally 200 years. As a consequence, there is some kind of name equation for just about everything. For example, the Carnot cycle, Joule-Thompson expansion, Helmholtz free energy, and the Gibbs (not the Redskins coach) free energy (even though in some cases, one name equation is just a derivative of another). Other prominent names you will see come up include Kelvin (or Lord Kelvin in some books), Clausius etc... I kid you not, it will be hard to keep track of all these people and associated name equations. But I'd like you to consider the following quote by Poincare.

"The order in which these elements are placed is much more important than the elements themselves. If I have the feeling... of this order, so as to perceive at a glance, the reasoning as a whole, I need no longer fear lest I forget one of the elements, for each of them will take its alloted place in the array, and that without any effort of memory on my part"

Understand what you are doing and more importantly why. This will help you put this course into perspective. I will also try to weave a story through the course to help you remember the flow of ideas. I don't know if you are old enough to have watched Battlestar Galactica on TV but there was this one episode where Starbuck (I think) teaches a group of kids on some planet how to carry out some plan against the cylons by remembering words to a song. It's the same sort of idea here.

I encourage everyone to work problems, the more the better. It will help you put the concepts being discussed on a firmer basis. There is a saying that goes "If you're going to talk the talk, you gotta walk the walk". You will discover that I have an unusual affinity for this quote. Also, when working problems, be aware of your problem's environment. Know exactly what conditions and assumptions are being made (constant volume, constant pressure, temperature etc...). There are too many ways you can go wrong if you don't know what you need to do and more importantly what sort of equation you have to use.

Get a scientific calculator and become familiar with how to use it. I had one HP-21S calculator for over ten years since my undergrad days. This thing was solid. Sadly they don't build things like they used to anymore so my new HP from Walmart feels pretty cheap. Also because thermodynamics, in particular, is an old field people like to work in old units. So units like the atmosphere or millimeters of mercury or bar are more common than SI units. However, you must be ready to convert between the two with ease. This will come with practice.

Finally, last but not least, four important points. This is the first (now second) time that I have taught this course and more specifically, taught to undergraduates. Please bear with me while I get my feet wet (still applies). Second, I will try and post my class notes on my web page. You can then download them from there. There is a chance that I will just print them out and hand them out each time but this will depend on how hectic the semester becomes. Third, although the textbook for this class is McQuarrie, I have never used McQuarrie for thermodynamics, or kinetics and upon glancing through the material decided that I didn't like how he presented things (still true). Just be aware that I may be coming from left field relative to McQuarrie on some days. Finally, I encourage everyone to look at different text books. Sometimes one author will confuse you and another will explain it differently in a clear manner. This applies to me as well. A little outside reading goes a long way.

Now why bother

Here we discuss why one studies thermodynamics (and kinetics and statistical mechanics). Quantum mechanics and thermodynamics are two pillars of chemistry. Quantum as you have just seen is concerned with the microscopic properties of atoms, molecules. In fact, if you think about it all the problems you have worked in quantum, whether it be the particle in a box, the harmonic oscillator, the rigid rotor deals with one box, one oscillator, one rotor. This is the single atom, single molecule limit. From these model systems you found the electronic energies of the system, the vibrational and rotational energies. You also found the wavefunctions whether you really cared about them or not. You may even have (don't know how far you got, actually I do since I taught 321 last semester) have modeled transitions between these levels using time dependent perturbation theory.

Thermodynamics, on the other hand, deals with ensembles or macroscopic quantities of matter. We're talking Avogadros number of atoms or molecules. It deals with energy conservation and energy transfer (the conversion between energy in its different forms such as kinetic energy and potential energy and its exchange from one body of matter to another), such as in chemical reactions. More importantly from a practicing chemist's point of view it predicts the spontaneous direction of chemical reactions or processes. Hey, if you mix A and B together do they react? Wouldn't you like to know beforehand? However, it does not presume a microscopic picture of molecules or atoms. In this sense thermodynamics is a self consistent field. Recall that thermodynamics was developed a long time ago in the context of engineers, inventors and others trying to make better steam engines or hot air balloons. But the results were so general that it worked with chemistry and physics as well.

Although thermodynamics tells you if something can happen it says nothing about how fast the process occurs. You don't know the rate of the process. This is the realm of chemical kinetics which we will discuss after establishing the basic principles of thermodynamics. Finally tying the macroscopic and microscopic pictures of matter together is the field of statistical mechanics. It uses statistical principles and a quantum mechanical view of atomic and molecular energy levels to tell you why a macroscopic thermodynamic quantity takes the value that it does.

Finally you should be aware that there are a number of approaches for teaching thermodynamics. One approach (I'll call it the classical approach) just teaches you the fundamental laws of thermodynamics, the behavior of gases, liquids and solids (without specifying any details of the system). You then do kinetics and usually there is a separate class for statistical mechanics (if any). The other tries to teach thermodynamics from a statistical mechanics approach (this is what McQuarrie is trying to do).

Chapter 4

Relevant Reading in McQuarrie

- Math review: pg 683-689
- Ideal gas equation of state: Ch.16, pg 637-642
- Real gas equation of state: Ch. 16, pg 642-648
- 1st Law of Thermodynamics:
  Hess Law and thermochemistry Ch. 19, pg 765-800 (Ignore 19-6)
- Entropy and the 2nd Law of Thermodynamics, Ch 20, pg 817-844 (Ignore 20-5, 20-8, 20-9)
- Entropy and the 3rd Law of Thermodynamics, Ch 21, pg 853-870, (Ignore 21-6)
- Spontaneity and Gibbs free energy, Ch 22, pg 881-910
- Single component phases, Ch. 23, pg 925-945, (Ignore 23-5)
- Mixtures, Ch. 24, pg 963-998
- Equilibrium, Ch. 26, pg 1049-1087, (Ignore 26-8, 26-9)
- Kinetics, Ch. 29, pg 1181-1213, (Ignore 29-7)
- Statistical mechanics, series and limits, MathChapter I, pg 723-726
- Statistical mechanics, Stirlings approximation, MathChapter J, pg 809-813

- Statistical mechanics, Boltzmann, Ch. 17, pg 693-716 and Section 20-5, pg 829-832
- Statistical mechanics, partition functions, ideal gases, Ch. 18, pg 731-756

Chapter 5

Summary of common equations

- Boyle's Law, Pressure/Volume inverse relation
- Charles' Law, Volume/Temperature direct relation
- Ideal gas Law, Boyle and Charles Laws put together, $pv = nRT$
- Dalton's Law, partial pressures of ideal gas, $p_{tot} = p_1 + p_2$ or more if greater that 2 components
- PV work (w), gas expansion work due to volume change against an external pressure
- Heat (q), the name says it all
- 1st Law of thermodynamics, Basically conservation of energy, $U = q + w$
- Joule-Thompson coefficient, associated with Joule expansion and change of temperature with change of pressure
- Enthalpy, $H = U + pV$
- Hess' Law, Thermochemistry and enthalpy bookkeeping
- Kirchoff's Equation, Get enthalpy at different temperatures through C_p
- no-name1, Get internal energy at different temperatures through C_v

- Fundamental equations of thermodynamics, Remember "Save that ship Gibbs", you'll see
- Maxwell's Relations, a consequence of the above
- Gibbs free energy, $G = H - TS$ or $G = A + pV$, constant Pressure and Temperature
- Helmholtz free energy, $A = U - TS$, constant Volume and Temperature
- Gibbs-Helmholtz equation, temperature dependence of ΔG
- no-name2, pressure dependence of ΔG
- Clapeyron equation, solid/liquid line in a phase diagram
- Clausius-Clapeyron equation, liquid/vapor line in a phase diagram (basically an extension of the Clapeyron equation)
- Trouton's Rule, $\Delta S = \frac{\Delta H_{vap}}{T_b}$ at liquid vapor line, nearly const value for many systems
- Gibbs-Duhem equation, The chemical potential of components in a mixture are not independent.
- Raoult's Law, relation between partial pressure of components in a mixture with its mole fraction
- Henry's Law, corrected Raoult, take that!
- Le'Chatelier's Principle, more products or reactants by varying pressure, temperature, concentration etc...
- Van't Hoff Equation, describes variation of the equilibrium constant. It is also basically the Gibbs Helmholtz equation.

As you are going through the course, periodically look through this section to help you remember these equations. Also if I have missed an equation just add it by hand here.

Chapter 6

Summary of common symbols

- q, heat
- w, work
- p, pressure
- V, volume
- n, moles
- T, temperature
- C_p, constant pressure, heat capacity
- C_v, constant volume, heat capacity
- U, internal energy
- H, enthalpy
- G, Gibbs free energy
- A, Helmholtz free energy
- S, entropy
- μ, chemical potential
- f, fugacity

- a, activity
- χ, mole fraction

Chapter 7

Units

Pressure

The SI unit of pressure is Pa (Pascal)

$$Pa = N/m^2 = J/m^3 = kg/ms^2$$

Misc. units

$$\begin{aligned} J &= kg \cdot \frac{m^2}{s^2} \\ J &= N \cdot m \\ N &= \frac{kg \cdot m}{s^2} \\ J &= Pa \cdot m^3 \end{aligned}$$

More common units

Common (practical) units of pressure are

- atm (atmosphere), basically you live at 1 atm pressure
- torr
- mm Hg (millimeters of mercury)
- bar

Pressure in Everyday Life

So that you are calibrated in terms of pressures, here is a list that I found on a BBC website.

- 10-20 atm - The pressure in space-vacuum
- 10-16 atm - The lowest pressure ever achieved by a man made gizmo
- 10-6 atm - Ordinary vacuum pumps
- 10-2 atm - The pressure in a common light bulb
- 0.5 - 1.5 atm - Atmospheric pressure
- 1.5 - 2.4 atm - Car tyres
- 3 - 7 atm - Flatus (!)
- 4 - 12 atm - Bicycle tyres
- 10 atm - The pressure inside the cylinder cavity in a car's engine
- 100 - 500 atm - Compressed gas cylinders
- 500 atm - The impact pressure of a karate fist punch (so what would Chuck Norris' value be?)
- 1000 atm - The pressure at the bottom of the Mariana Trench
- 7000 atm - Water compressors
- 106 atm - The pressure at the centre of the earth, and also the highest pressure ever achieved by a man-made machine (diamond anvil)
- 1011 atm - The pressure at the centre of the sun -enough to ignite fusion reactions
- Approx. 1029 atm - The pressure at the centre of a neutron star.

Unit conversion

- 1 atm $= 1.01325 \times 10^5$ Pa
- 1 atm $=$ 760 torr
- 1 atm $=$ 760 mm Hg

- 1 atm = 1.01325 bar

where

- 1 mm Hg = 1 Torr
- 1 bar = 10^5 Pa

Volume

The SI unit of volume is the cubic meter (m^3). Of course this means that no one uses this.

More common units

Common (practical) units of volume are

- cm^3 (aka “cc” where 1 cc = 1 mL in case you watch these medical shows on TV)
- dm^3
- L, liters

Unit conversion

- 1 L = $1dm^3$
- 1 L = $1000cm^3$
- 1 L = $1 \times 10^{-3}m^3$

Temperature

The SI unit of temperature is Kelvin (K). Sometimes you will see Celsius. But it’s more common to use Kelvin.

$$K = C + 273.15 \tag{7.1}$$

Ideal gas constant, R

- $R = 8.314 J/mol \cdot K$, this is very commonly used
- $R = 0.08206 L \cdot atm/mol \cdot K$, this is also very commonly used
- $R = 8.314 kg \cdot m^2/s^2 \cdot mol \cdot K$
- $R = 8.314 kPa \cdot dm^3/mol \cdot K$
- $R = 1.9872 cal/mol \cdot K$
- $R = 0.083145 L \cdot bar/mol \cdot K$

Energy

- 1 cal = 4.18 J
- 1 kcal = 4.18 kJ
- Joules

Demo

A demo can be shown here by burning donuts or burning potato chips and heating a water bath and watching the temperature change. Pringles burn fairly cleanly. Doritos don't burn as well. If you're going to do this, I recommend using a hood.

Some examples of unit conversion

To get warmed up, convert the following

Example 1

Calculate R in terms of calories starting with $R = 8.314 J/mol \cdot K$.

Ans:

$$1 cal = 4.184 J$$

By the way 1 real world "calorie" is actually 1 scientific kcal. So if you ever watch the movie "Supersize me" you will see that our health officials have forgotten their units. No wonder we're so huge.

$$\frac{8.314}{4.184} = 1.9871 cal/mol \cdot K$$

$$R = 1.9871 cal/mol \cdot K$$

Example 2

Calculate R in terms of bar and L starting with $R = 8.314 J/mol \cdot K$
Ans: $1 Joule = 1 Pa \cdot m^3$ We have

$$R = 8.314 Pa \cdot m^3/mol \cdot K$$

Now recall that $1 Pa = 10^{-5} bar$. We now have

$$R = 8.314 \times 10^{-5} bar \cdot m^3/mol \cdot K$$

where $1m^3 = 1000L$. Now we get

$$R = 8.314 \times 10^{-2} bar \cdot L/mol \cdot K$$

The desired answer is

$$R = 0.08314 bar \cdot L/mol \cdot K$$

Example 3

Calculate R in terms of $L \cdot atm$ starting with $R = 8.314 J/mol \cdot K$.
Ans: $J = Pa \cdot m^3$ giving

$$\frac{R = 8.314 Pa \cdot m^3}{mol \cdot K}$$

where $1.01325 \times 10^5 Pa = 1 atm$ or $1 Pa = 9.87 \times 10^{-6} atm$. This gives

$$R = 8.314(9.87 \times 10^{-6}) atm \cdot m^3/mol \cdot K$$

where $1m^3 = 1000L$ giving

$$8314(9.87 \times 10^{-6}) L \cdot atm/mol \cdot K$$

$$R = 0.08206 L \cdot atm/mol \cdot K$$

Chapter 8

Math interlude

Exact or total differentials

These types of differentials are important because they illustrate the idea of path independency. This is an important concept when working with thermodynamic functions such as energy, enthalpy and entropy. These thermodynamic functions are called state functions and they are said to depend only on the initial and the final state of the system and not the path traversed in going from one to the other.

Assume a function of two variables $f(x, y)$. In reality, this could be a function depending on actual variables [say (V, T), (P, T) etc...]. Now the total differential of this function $f(x, y)$ is written as

$$\boxed{df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy} \tag{8.1}$$

where the subscripts x and y refer to keeping x or y constant while differentiating. The total differential describes how the function f will change when both x and y change. The homework will include an example that will better drive home this point in a physical way.

Now, since $\left(\frac{\partial f}{\partial x}\right)$ and $\left(\frac{\partial f}{\partial y}\right)$ are functions of x and y one may also write

$$df = M(x, y)dx + N(x, y)dy.$$

If we form second derivatives of the function $f(x, y)$ there are several possibilities. For example, $\left(\frac{\partial f}{\partial x}\right)$ can be differentiated with respect to either x or y. Likewise $\left(\frac{\partial f}{\partial y}\right)$ can be differentiated with respect to either x or y. We then get the following second derivatives

- $\frac{\partial^2 f}{\partial x^2}$
- $\frac{\partial^2 f}{\partial x \partial y}$
- $\frac{\partial^2 f}{\partial y^2}$
- $\frac{\partial^2 f}{\partial y \partial x}$

However, of these four terms only three are actually distinct. In this respect, it can be shown that for a function of several variables that the order of differentiation with respect to 2 variables such as x, y does not matter and that

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

or that

$$\begin{aligned} \frac{\partial M}{\partial y} &= \frac{\partial^2 f}{\partial y \partial x} \\ \frac{\partial N}{\partial x} &= \frac{\partial^2 f}{\partial x \partial y} \end{aligned}$$

and that

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}.$$

These are important tests of what is called exactness. We will use this later in deriving what are referred to as Maxwell's relations (no, not the Electricity and Magnetism ones).

Now conversely a differential expression

$$M(x, y)dx + N(x, y)dy$$

is called an exact differential if it happens to correspond to the total differential of some function f(x,y). Let's say you don't know f(x,y) a priori. Then to check, the necessary condition for this random differential to be exact is if

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}.$$

Example

The state of a thermodynamic system is generally a function of more than one independent variable. Generally, many thermodynamic problems you will encounter involve only two independent variables (P,T) or (V,T) etc... Consider the case of an ideal gas where, without deriving it yet and simply asking you to remember Freshman chemistry -this is the ideal gas equation),

$$\begin{aligned} pV &= nRT \\ V &= f(T,p) \\ V &= \frac{nRT}{p} \\ V &= \frac{RT}{p}(n=1). \end{aligned}$$

V can therefore be written as a function of T and p since R is a constant. Its total or exact differential is

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT$$

which explicitly shows its dependence on p and T.

Now let's evaluate $\left(\frac{\partial V}{\partial p}\right)_T$ and $\left(\frac{\partial V}{\partial T}\right)_p$. We get

$$\begin{aligned} \left(\frac{\partial V}{\partial p}\right)_T &= -\frac{RT}{p^2} \\ \left(\frac{\partial V}{\partial T}\right)_p &= \frac{R}{p} \end{aligned}$$

giving

$$dV = \frac{-RT}{p^2}dP + \frac{R}{p}dT$$

You can now check for exactness in your leisure time.

Math games

Often in thermodynamics there will be no convenient experimental method for evaluating a dependency (i.e. derivative needed for some problem). In this case, we can play some math games to get what we want.

Example

Start with the total differential for $V = f(p, T)$

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT$$

Say you want or need $\left(\frac{\partial p}{\partial T}\right)_V$. To obtain this dependency, divide both sides by dT and keep V constant (i.e. $dV = 0$).

$$\left(\frac{dV}{dT}\right)_V = \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{dp}{dT}\right)_V + \left(\frac{\partial V}{\partial T}\right)_p = 0$$

Since $dV = 0$, we have

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T},$$

which is the expression we were after. Note that the numerator on the right is related to what is called the coefficient of thermal expansion (α) while the denominator is related to what is called the coefficient of compressibility (κ).

Example

Next, starting with the same total differential above

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_p dT$$

say you want $\left(\frac{\partial T}{\partial p}\right)_V$. To obtain this, divide by dp and keep V constant (i.e. $dV = 0$). We get

$$\left(\frac{dV}{dp}\right)_V = \left(\frac{\partial V}{\partial p}\right)_T + \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{dT}{dp}\right)_V = 0,$$

resulting in

$$\left(\frac{\partial T}{\partial p}\right)_V = -\frac{\left(\frac{\partial V}{\partial p}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_p},$$

which is our desired expression.

Example, the inverter

From the previous two results we can then see that

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{1}{\left(\frac{\partial T}{\partial p}\right)_V}.$$

This relationship has a name in some texts and is called the "inverter". Generally speaking then

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}}. \tag{8.2}$$

Example, the cyclic rule or Euler chain relation

Another useful relation between partial derivatives is called the cyclic rule. The total differential of a function is written (again) as

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = 0$$

this time using $z = f(x, y)$. Furthermore, as before, we restrict the previous equation to those where variations of x and y leave the value of z unchanged $z(x, y) = \mathit{constant}$ or conversely $(dz = 0)$.

$$\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = 0.$$

Dividing by dy and keeping z constant, we get

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x = 0$$

At this point, multiply by $\left(\frac{\partial y}{\partial z}\right)_x$, using our previous inverter relation, to get

$$\left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + 1 = 0.$$

This yields our final result

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1}. \tag{8.3}$$

Note that it can also be shown that

$$\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z = -1.$$

This is useful since x,y,z in the numerator are related the y,z,x in the denominator as well as to the associated subscripts by a cyclic permutation. Since in many thermodynamic situations the variables of state are functions of 2 other variables there is frequent use of such relations.

You don't have to memorize this equation. Just write down x,y,z in the numerator in any order. Usually just keep the x,y,z order. Then underneath in the denominator write down x,y,z in any order but do not repeat the the same letter in both the numerator and denominator. You will find that there are only two unique combinations (those shown above).

Summary

Relation 1

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \tag{8.4}$$

Relation 2 (the "inverter")

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \tag{8.5}$$

Relation 3 (the "permuter")

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \tag{8.6}$$

Relation 4 (the "Euler chain relation")

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{8.7}$$

Solving the differential

Given the total differential for $f(x, y)$

$$\begin{aligned} df &= \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \\ &= M dx + N dy \end{aligned}$$

its functional form can be found in the following systematic fashion.

From $\frac{\partial f}{\partial x} = M$ integrate to get

$$f = \int M dx + k(y)$$

where $k(y)$ is some constant that potentially depends on y. The next step is to find out what $k(y)$ is by differentiating this expression with respect to y.

$$\left(\frac{\partial f}{\partial y}\right)_x = \frac{\partial}{\partial y}\left(\int M dx\right) + \frac{d}{dy}k(y) = N(x, y).$$

Now we rearrange and find $k(y)$ by integrating $\frac{dk(y)}{dy}$

$$\frac{dk(y)}{dy} = N(x, y) - \frac{\partial}{\partial y}\left(\int M dx\right)$$

to get

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

Replace this $k(y)$ into our previous expression for f to get what we were after

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

Example

Solve

$$df = (x^3 + 3xy^2)dx + (3x^2y + y^3)dy = 0.$$

Test for exactness

$$\begin{aligned} M(x,y) &= x^3+3xy^2 \\ N(x,y) &= 3x^2y+y^3 \end{aligned}$$

taking their cross derivatives we get

$$\frac{\partial M}{\partial y} = 6xy$$
$$\frac{\partial N}{\partial x} = 6xy$$

Hence the equation is exact. Now, we go after $f(x,y)$

$$\begin{aligned} f &= \int M dx + k(y) \\ &= \int (x^3+3xy^2)dx + k(y) \\ &= \frac{x^4}{4} + \frac{3y^2x^2}{2} + k(y). \end{aligned}$$

Find $k(y)$ by differentiating this, keeping x constant

$$\left(\frac{\partial f}{\partial y}\right)_x = \frac{6yx^2}{2} + \frac{dk(y)}{dy} = N(x,y)$$

Therefore, we have the equivalence

$$\begin{aligned} \frac{6yx^2}{2} + \frac{dk(y)}{dy} &= 3x^2y+y^3 \\ \frac{dk(y)}{dy} &= y^3 \end{aligned}$$

yielding

$$k(y) = \frac{y^4}{4} + const$$

Put it all together now.

$$f(x,y) = \frac{x^4}{4} + \frac{3x^2y^2}{2} + \frac{y^4}{4} + const$$

Integrating factors

The idea behind this method is simple. We sometimes have an equation

$$p(x,y)dx + q(x,y)dy = 0$$

that is not exact. However, if we multiply it by some suitable function f(x,y), the new equation

$$fpdx + fqdy = 0$$

is exact so that it can be solved like we did before. Our job here is to find this integrating factor $f(x$,$y)$.

In simple cases, $f(x,y)$, can be found by inspection but more generally do the following. Since

$$fpdx + fqdy = 0$$

is exact

$$\frac{\partial fp}{\partial y} = \frac{\partial fq}{\partial x}$$

In general, this is complicated. Therefore make some simplifications and look for an integrating factor that depends only on one variable. Thus let $f = f(x)$.

$$f\frac{\partial p}{\partial y} + p\frac{\partial f}{\partial y} = f\frac{\partial q}{\partial x} + q\frac{\partial f}{\partial x}$$

where the second term on the left is zero because f has no y dependence. We then get

$$f\frac{\partial p}{\partial y} = f\frac{\partial q}{\partial x} + q\frac{\partial f}{\partial x}$$

Divide through by fq to get

$$\frac{1}{q}\frac{\partial p}{\partial y} = \frac{1}{q}\frac{\partial q}{\partial x} + \frac{1}{f}\frac{\partial f}{\partial x}$$

Now consolidate terms to get

$$\begin{aligned}
\frac{1}{f}\frac{\partial f}{\partial x} &= \frac{1}{q}\left(\frac{\partial p}{\partial y} - \frac{\partial q}{\partial x}\right) \\
lnf &= \int \frac{1}{q}\left(\frac{\partial p}{\partial y} - \frac{\partial q}{\partial x}\right) dx
\end{aligned}$$

The desired integrating factor is therefore

$$f = e^{\int \frac{1}{q}\left(\frac{\partial p}{\partial y} - \frac{\partial q}{\partial x}\right)} \tag{8.8}$$

Note that the same type of argument can be made if one assumes $f = f(y)$ only rather than $f = f(x)$ as done here.

Linear differential equations

This section is mostly for the kinetics part of this course.

A 1st order differential equation is said to be linear if it can be written

$$y^{'} + p(x)y = r(x)$$

The characteristic feature of the equation is that it is linear in y and $y^{'}$ whereas p and r on the right may be any function of x.

Now if $r(x) = 0$ the equation is said to be homogeneous. If $r(x) \neq 0$ then this is a non-homogeneous equation.

Homogeneous case

For example

$$\begin{aligned} y^{'} + p(x)y &= 0 \\ \frac{dy}{dx} &= -p(x)y \\ \frac{dy}{y} &= -p(x)dx \\ lny &= -\int p(x)dx + const \end{aligned}$$

resulting in

$$y = Ae^{-\int p(x)dx}$$

where A is a constant. This is the desired general solution for the homogeneous case.

Non-homogeneous case

Consider the same equation

$$y^{'} + p(x)y = r(x)$$

This will be solved by using an integrating factor. Rewrite the expression as

$$\begin{aligned}
\frac{dy}{dx} + p(x)y - r(x) &= 0 \\
dy + (p(x)y - r(x))dx &= 0 \\
(p(x)y - r(x))dx + dy &= 0 \\
Pdx + Qdy &= 0
\end{aligned}$$

where

$$\begin{aligned}
P &= p(x)y - r(x) \\
Q &= 1
\end{aligned}$$

From our integrating factor formula derived previously

$$\begin{aligned}
\frac{1}{f}\frac{df}{dx} &= \frac{1}{q}\left(\frac{\partial p}{\partial y} - \frac{\partial q}{\partial x}\right) \\
\frac{1}{f}\frac{df}{dx} &= \frac{1}{1}\left(\frac{\partial (p(x)y - r(x))}{\partial y} - 0\right) \\
\frac{1}{f}\frac{df}{dx} &= \frac{\partial [p(x)y - r(x)]}{\partial y} \\
\frac{1}{f}\frac{df}{dx} &= p(x) \\
\frac{df}{f} &= \int p(x)dx \\
lnf &= \int p(x)x + const \\
f &= Ae^{\int p(x)dx}
\end{aligned}$$

or if $A = 1$

$$f(x) = e^{\int p(x)dx}$$

This is our desired integrating factor. Now multiply our original equation by this integrating factor to make it exact.

$$\begin{aligned} f(x)[y^{'} + p(x)y] &= f(x)r(x) \\ e^{\int pdx}(y^{'} + py) &= e^{\int pdx}r(x) \\ \left(e^{\int pdx}\right)^{'} &= e^{\int pdx}r(x) \end{aligned}$$

You can check for yourself that the last expression is true.

$$\begin{aligned} \left(e^{\int pdx}\right)^{'} &= e^{\int pdx}y^{'} + y\frac{d}{dx}(e^{\int pdx})\frac{d(\int pdx)}{dx} \\ &= e^{\int pdx}y^{'} + ye^{\int pdx}p \\ &= e^{\int pdx}(y^{'} + yp) \end{aligned}$$

So you can see that the expression checks out.

Back to where we left off

$$\left(e^{\int pdx}\right)^{'} = e^{\int pdx}r(x)$$

Integrate this with respect to x

$$e^{\int pdx}y = \int e^{\int pdx}r(x)dx + const$$

giving

$$y = e^{-\int pdx}\left[\int e^{\int pdx}r(x)dx + const\right]$$

This is our desired final solution. The choice of constant does not matter.

Example

Nonhomogeneous 1st order linear differential equation.

Solve the following linear differential equation.

$$y^{'} - y = e^{2x}$$

Here

$$\begin{aligned} p(x) &= -1 \\ r(x) &= e^{2x} \end{aligned}$$

Solve for the exponential term

$$\begin{aligned} e^{\int p dx} &= e^{\int -1 dx} \\ &= e^{-x} \end{aligned}$$

We have

$$e^{\int p dx} = e^{-x}$$

Plug this into the general formula for the integrating factor.

$$\begin{aligned} y &= e^{-\int p dx}\left[\int e^{\int p dx} r(x) dx + const\right] \\ &= e^{x}\left[\int e^{-x} r(x) dx + const\right] \\ &= e^{x}\left[\int e^{-x} e^{2x} dx + const\right] \\ &= e^{x}\left[\int e^{x} dx + const\right] \\ &= e^{x}\left[e^{x} + const\right] \end{aligned}$$

Our general solution to the problem is therefore

$$y = Ce^{x} + e^{2x}$$

where C is a constant.

Chapter 9

Thermo definitions

- **System**: the system is the part of the world in which we have a special interest. It may be a reaction vessel, an engine, an electrochemical cell, a biological cell, etc...
- **Surroundings**: everything else
- **Open system**: if *matter* can be transferred through the boundary between the system and its surroundings
- **Closed system**: *matter* cannot pass through the boundary between the system and its surroundings. Both open and closed systems, however, can exchange energy with their surroundings. We will primarily deal with closed systems in this class.

Within closed systems we have two subclasses

- **Isolated system**: This is a closed system and on top of it, no mechanical or thermal energy can be exchanged between system and surrounding. This is boring and we will generally not be interested in this.
- **Adiabatic system**: This is also a closed system, but absolutely no thermal energy can be exchanged between the system and surrounding. However mechanical work or energy can be transfered (unlike the pure isolated system).

Some important processes as we move from some initial state of a system to a final state are characterized by holding a quantity constant during the process:

- **isobaric** means $\Delta p = 0$
- **isothermal** mean $\Delta T = 0$
- **isentropic** means $\Delta S = 0$
- **isometric** means $\Delta V = 0$
- **adiabatic** means $dq = 0$

Pictorial representations

I guess one day I'll add these drawings.

Chapter 10

Equation of state: Ideal gases

A system is in a definite state when all of its properties (e.g. mass, pressure, volume, temperature, etc...) have definite values. The state of the system is therefore described by specifying the values of some or all of its properties.

The question we ask is whether you need to specify 5, 20, 50, 100, different properties to ensure that the state is completely described. Fortunately only four properties, mass, volume, temperature, and pressure are ordinarily required.

The equation of state is the mathematical relationship between the values of these four properties. Unfortunately, of solids, liquids and gases, only the gas phase allows for a simple quantitative description of the equation of state.

Ideal gas equation

An ideal gas is defined as one in which all collisions between point particles (in reality, atoms or molecules but idealized here to be particles which occupy no volume) are perfectly elastic (no loss of energy on collision) and in which there are no intermolecular interactions whether attractive or repulsive. One can therefore visualize the ideal gas as a collection of infinitesimally small hard spheres which collide but which otherwise *do not* interact with each other. In such a gas, all the internal energy is in the form of kinetic energy and any change in internal energy is accompanied by a change in the temperature of the gas. Note that we say nothing about what this internal energy actually is. In fact, classical thermodynamics doesn't care. But you know from your previous classes that this internal energy is basically the rotational and vibrational energies of the system's constituent atoms or molecules. Furthermore, in the case of molecules there is additional energy tied up in the chemical bonds (whether ionic or covalent).

Definition: an ideal gas is one that obeys the following equation of state

$$\boxed{pV = nRT} \tag{10.1}$$

where n is the number of moles of gas and R is the ideal gas constant. Furthermore, the internal energy of the ideal gas, U, is a function of the temperature only. (note that some authors use E for internal energy, same thing) As a consequence, we say that U has no volume or pressure dependence

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \tag{10.2}$$

$$\left(\frac{\partial U}{\partial p}\right)_T = 0. \tag{10.3}$$

Note that I have simply asserted this for ideal gases. I will derive it later, however, remembering this little fact now will help a lot down the road.

In a microscopic sense this is saying that if you change the volume and pack the gas atoms closer together, they still do not interact. Likewise, changing the pressure does nothing either. The atoms or molecules are blissfully ignorant of each other.

Derivation

Now, the ideal gas equation of state can be derived from Boyle's Law and Charles' Law.

Boyle's Law

Recall that this is an expression derived in 1661 (or 1662) by Robert Boyle which describes an inverse relationship between pressure and volume. He supposedly discovered this in the context of hot air balloons or something but don't take my word on this. So at *constant temperature* and with a *constant amount of stuff* the pressure of a gas is inversely proportional to its volume. Consider squishing a balloon (actively reducing the volume occupied by the gas). Here the balloon's gas is our system of interest. Hence when we talk about p and V we are referring to its pressure and volume.

Now, as you compress the balloon the pressure exerted by the air inside increase dramatically. We have

$$p = \frac{const_1}{V}$$

or

$$pV = const_1.$$

Alternatively, we see that

$$\boxed{V = \frac{const_1}{p}}$$

from where you see that if p increases, V decreases.

Demo opportunity

One can do a demo here with a closed syringe. Plug up a disposable syringe. When one puts pressure on the plunger, the volume will decrease and will simultaneously increase the system's pressure. Conversely, decreasing the system's pressure will increase its volume. Again, the pressure we are talking about is the gas pressure inside the syringe.

In either the balloon example above or the disposable syringe demo, when you -the external agent of change- imposes your will on the system the system's gas responds. In both cases, we saw that the pressure increased. What I want to you be cognizant of at this point is that, when all is said and done, equilibrium is established between you and the system. Hence, the system's pressure will equal the pressure you are imposing on it. Think about it. If it didn't, you would be able to continue compressing the balloon or the syringe.

Charles' Law

Next, in 1787, French physicist Jacques Charles observed that the volume of a gas under *constant pressure* and *constant stuff* conditions increases or decreases with temperature (i.e. there exists a linear relationship between the volume and temperature of a system). Note that there are some books which call this temperature-volume relationship by the name of Gay-Lussac's Law. There are others which call it the Law of Charles and Gay-Lussac. This has to do with who published first (bottom line, if you're an academic, publish in a timely fashion.)

Thus, under constant pressure/stuff conditions, the hotter the gas is the more volume it occupies and vice versa.

$$\boxed{V = const_2(T)}.$$

Demo opportunity

One can do a demo here using a filled balloon and liquid nitrogen. Pour the liquid nitrogen over the balloon (don't do it the other way by trying to dunk the balloon into LN2. It takes longer and sometimes the balloon will freeze and crack letting all the air out.). As the gas inside cools, the balloon volume will decrease. Let the balloon warm up and it should expand again.

Avogadro's Law

Finally, there is a third relationship that we need. It is called Avogadro's law in some texts and what it says is that the volume of a gas is proportional to how much stuff is present (i.e. n). Note that implicit here is the idea that both the gas' temperature and pressure remain constant.

$$\boxed{V = const_3(n)}.$$

Putting Boyle and Charles and Avogadro together

Qualitatively

We now want to put all the empirically observed gas laws together. Qualitatively, this is pretty straightforward. We have just seen that the three laws say

$$\begin{aligned} V &= \frac{const_1}{p} \\ V &= const_2(T) \\ V &= const_3(n). \end{aligned}$$

If we just merge all three laws together you can see that in the numerator we will find n and T. In the denominator we will have p and all of this will be tied together with an overall constant of proportionality c that encompasses what is buried in $const_1$, $const_2$ and $const_3$. We have

$$V = \frac{cnT}{p}$$

which is basically the ideal gas law if $c = R$.

More formally

There is, however, a more formal way to derive the ideal gas equation of state. For a given amount of stuff n we see that V depends only on T and p.

$$V = f(T, p).$$

The total derivative of this function is then

$$dV = \left(\frac{\partial V}{\partial T}\right)_{n,p} dT + \left(\frac{\partial V}{\partial p}\right)_{n,T} dp$$

where recall for constant stuff and pressure, Charles says $V = const_2(T)$ and thus

$$\left(\frac{\partial V}{\partial T}\right)_{n,p} = const_2.$$

Next, recall for constant stuff and constant temperature, Bolye says that $V = \frac{const_1}{p}$ and thus

$$\left(\frac{\partial V}{\partial p}\right)_{n,T} = -\frac{const_1}{p^2}.$$

When all is put together we get

$$dV = const_2 dT - \frac{const_1}{p^2} dp.$$

We can simplify this more if we recall that

$$\begin{aligned} const_2 &= \frac{V}{T} \text{ (Charles' Law)} \\ const_1 &= Vp \text{ (Boyle's Law).} \end{aligned}$$

This gives

$$dV = \frac{V}{T} dT + \frac{-V}{p} dp.$$

Rearrange this to get

$$\frac{dV}{V} = \frac{dT}{T} - \frac{dp}{p}.$$

Integrate this to get

$$\ln V = \ln T - \ln p + const.$$

This simplifies to

$$\ln V = \ln \frac{T}{p} + const$$

or

$$V = \frac{T}{p} e^{const} = \frac{T}{p} const_{final}.$$

At this point, recall that we had a fixed amount of stuff, n. So the final constant of proportionality, $const_{final}$ includes n and by Avogadro's law we find that

$$V = nR\frac{T}{p}$$

provided that $const_{final} = nR$ with R the ideal gas constant. Our desired expression is then

$$pV = nRT.$$

Note that from here on out when working with the ideal gas equation of state you will usually have pressures in terms of atm. Volumes will often be in terms of liters, n is in moles, and T is in Kelvin.

Demo opportunity

A demo of the ideal gas law can be done here. At standard temperature and pressure (STP -no not the stuff you get at AutoZone) which is 1 atm and 273.15 K one mole of gas occupies 22.4 L. This can be demonstrated by filling a small Erlenmeyer with 1 mol of liquid nitrogen. When the density of liquid nitrogen and the molar mass are accounted for half a mole of LN2 is about 17.5 mL. Then put a balloon on top of the Erlenmeyer. Warm up the liquid nitrogen by putting it in a warm water bath. You will see the balloon expand. Measure the radius of the balloon and from geometric considerations calculate the balloon volume in liters.

Example, easy

Calculate the volume occupied by 1 mol of an ideal gas at 25^{o}C and 1 atm.

Ans:

$$\begin{aligned} pV &= nRT \\ (1)(V) &= (1)(0.08206)(298.15) \end{aligned}$$

We get

- $V = 24.47$ L
- $V = 24470$ mL
- $V = 24470 cm^3$

Example

How many grams of oxygen (O_2) are there in a 50 L tank at 21^{o}C when the oxygen pressure is 15.7 atm.

Ans:

$$\begin{aligned} pV &= nRT \\ (15.7)(50) &= n(0.08206)(294.15) \end{aligned}$$

leaving $n = 32.52$ mol oxygen. The molecular weight of O_2 is 32 grams/mole giving 1.04 kg O_2 present in the tank.

Example

What is the pressure of a 50L tank containing 3.03 kg oxygen at 23^{o}C?

Ans: The number of moles of oxygen is $n = 94.48$. Next

$$\begin{aligned} pV &= nRT \\ p(50) &= (94.68)(0.08206)(296.15) \end{aligned}$$

From this we get $p = 46$ atm.

Example, harder

In some industrial process, N_2 is heated to 500K in a vessel of constant volume (sounds dangerous). It enters the vessel at a pressure of 100 atm and at $T = 300K$. What pressure would it exert at the working temperature if it behaved as an ideal gas.

Ans:

$$\begin{aligned} pV &= nRT \\ p_2V_2 &= (nR)(500) \end{aligned}$$

where we want p_2 and note that the volume is constant

$$p_1V_1 = (nR)(300)$$
$$p_2V_2 = (nR)(500).$$

Therefore, the ratio is

$$\begin{aligned} \frac{p_2V_2}{p_1V_1} &= \frac{500}{300} \\ \frac{p_2}{p_1} &= \frac{5}{3} \\ \frac{p_2}{100} &= \frac{5}{3}. \end{aligned}$$

We then get our desired answer

$$p_2 = 167 \text{ atm}.$$

Example

Alternatively, (using the same information given in the previous example) what temperature would result in the sample exerting a pressure of 300 atm.

Ans:

$$\begin{aligned} p_1V_1 &= (nR)T_1 \\ p_2V_2 &= (nR)T_2 \end{aligned}$$

where recall again that the volume stays constant. Thus

$$\begin{aligned} \frac{p_1}{p_2} &= \frac{T_1}{T_2} \\ \frac{100}{300} &= \frac{300}{T_2}. \end{aligned}$$

From this we see that $T_2 = 900$ Kelvin.

Dalton's Law

Simply stated, Dalton's law says that the pressure exerted by a mixture of ideal gases is the sum of their individual partial pressures.

$$p_{tot} = p_1 + p_1 + \dots$$

The partial pressure is defined as the pressure of a single ideal gas in the mixture as if that gas were alone in the container. In other words, Dalton maintained that since there was an enormous amount of space between the gas molecules within the mixture that the gas molecules did not have any influence on the motion of other gas molecules, therefore the pressure of a gas sample would be the same whether it was the only gas in the container or if it were among other gases. This assumption that molecules act *independently* of one another works fine as long as the gases are ideal. For real gases, it works provided that there is a lot of space between the component gas molecules in the mixture and the temperature is not too low. Lowering the temperature and/or compressing the gas will upset this assumption.

Example

A 10L container holds 1 mole N_2, 3 moles of H_2 at 298K. What is the total pressure in atmospheres if each component behaves as an ideal gas.

Ans:

$$\begin{aligned} p_{N_2} &= \frac{(1)RT}{V} \\ p_{H_2} &= \frac{(3)RT}{V} \end{aligned}$$

The total pressure is the sum of each component in the mixture

$$\begin{aligned} p_{tot} &= p_{N_2} + p_{H_2} \\ &= \frac{RT}{V}(1+3) \\ &= \frac{4(0.08206)(298)}{10} \\ &= 9.78 \text{ atm} \end{aligned}$$

Partial pressures and mole fraction

Finally, it is possible to relate the partial pressure of a gas in a mixture to its mole fraction χ. Namely, the ratio of the partial pressure of one component of a gas mixture to the total pressure is

$$\begin{aligned}\frac{p_1}{p_{tot}} &= \frac{\left(\frac{n_1RT}{V}\right)}{\left(\frac{n_1RT}{V}+\frac{n_2RT}{V}+\ldots\right)}\\ &= \frac{\left(\frac{n_1RT}{V}\right)}{(n_1+n_2+\ldots)\frac{RT}{V}}\\ &= \frac{n_1}{n_1+n_2+\ldots}\end{aligned}$$

Therefore

$$\boxed{\frac{p_1}{p_{tot}} = \chi_1} \tag{10.4}$$

Thus the ratio of partial pressure to total pressure is equal to the mole fraction of the gas in the mixture.

Alternatively, the partial pressure of an ideal gas could just as well have been defined as

$$\boxed{p_1 = \chi_1 p_{tot}} \tag{10.5}$$

and likewise

$$\begin{aligned}p_2 &= \chi_2 p_{tot}\\ p_3 &= \chi_3 p_{tot}\\ &\text{etc}\ldots\end{aligned}$$

Chapter 11

Equation of state: Real gases

Real gases do not obey the ideal gas law. Deviations from ideal behavior are particularly important at high pressures and low temperatures. Therefore to develop a better equation of state for "real" gases the Van der Waals equation was introduced in 1873 (or 1877, depends on who you believe in but nonetheless highlights the fact that this was a long time ago). The van der Waals equation does not assume like the ideal gas law that we are dealing with point particles that do not interact except through elastic collisions. It corrects for the fact that in reality molecules are not point particles but rather occupy some volume (this means van der Waals messed around with the V in the ideal gas equation). Next the van der Waals equation accounts for the fact that gas molecules attract one another when close enough and hence that real gases are more compressible. These attractive forces are still referred to today as van der Waals forces. (basically this also means that van der Waals messed with the p term in the ideal gas equation)

The van der Waals forces we have learned about previously are

- Dipole-dipole (Keesom 1912)
- Dipole-induced dipole (Debye 1920)
- Dispersion Forces (London 1930)

I'll assume that you remember what the idea behind these interactions were.

You can see evidence of nonideal gases everywhere. Add enough pressure and the gas condenses to a liquid or a solid. For example, if you work in a chemistry lab, chances are that you use liquid nitrogen for the trap on your vacuum line. If you are a physicist you use liquid helium to cool your samples to low temperatures. If you watch movies where you have bubbling solutions made by the mad scientist, that's solid carbon dioxide (aka dry ice) at work. These all show that real gases are non-ideal.

These are the corrections made by van der Waals to the ideal gas equation of state.

Volume correction

Real molecules are not point particles.

$$V_m \to (V_m - b)$$

where b is the volume per mole occupied by real molecules. Note that V_m is the molar volume of the gas.

Pressure correction

Real molecules interact with one another.

$$p \to \left(p + \frac{a}{V_m^2}\right)$$

where a is some constant. Again V_m is the molar volume of the gas.

Summary

The ideal gas equation thus gets transformed into the van der Waals equation of state

$$pV = nRT \to \left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT.$$

This gives

$$\boxed{\left(p + \tfrac{a}{V_m^2}\right)(V_m - b) = RT} \tag{11.1}$$

and is for one mole of real gas. A more general expression for n moles of real gas is

$$\boxed{\left(p + \tfrac{n^2 a}{V^2}\right)(V - nb) = nRT}. \tag{11.2}$$

Finally, there are tables of van der Waals a and b coefficients. Here is a sampling of them.

Gas	a ($L^2 \cdot atm/mol^2$)	b (L/mol)
He	0.0342	0.02370
Ne	0.211	0.0171
Ar	1.35	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0511
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
H_2O	5.46	0.0305
CH_4	2.25	0.0428
CO_2	3.59	0.0427
CCl_4	20.4	0.1383

Summary of other real gas equations

Now it goes without saying that over the years people have thought of other ways to better model real gases. There are a ton of equations that are listed below that show you what they have tried. Some look easier than others. Nevertheless, the van der Waal expression is pretty decent and is very commonly used, although it should be said that the ideal gas equation isn't bad either under some circumstances. I assume you are able to tell yourself what those circumstances are.

van der Waals equation

It was the first to describe deviations for ideality

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT \tag{11.3}$$

where V_m is the volume/mole and a and b are the above gas specific constants.

Berthelot equation

This is too unwieldy to be used generally and as an equation of state. However, it is convenient in calculations of deviations from ideality near 1 atm pressure

$$\left(p + \frac{a}{TV_m^2}\right)(V_m - b) = RT. \tag{11.4}$$

Again a and b are constants that you go and look up in a table. Note that these constants are not the same as those in the van der Waals equation of state.

Redlich-Kwong equation

This was first proposed back in 1949 (still a while ago)

$$\left[p + \frac{a}{\sqrt{T}V_m(V_m + b)}\right](V_m - b) = RT. \tag{11.5}$$

As usual, a and b are constants, characteristic of the gas, that you go look up in a table somewhere.

Dieterici equation

$$p(V_m - b) = RTe^{\frac{-a}{RTV_m}} \tag{11.6}$$

Beattie-Bridgeman equation

$$pV_m^2 = (1 - \gamma)RT(V_m + \beta) - \alpha \tag{11.7}$$

where $\alpha = a_0\left(1 + \frac{a}{V_m}\right)$, $\beta = b_0\left(1 - \frac{b}{V_m}\right)$ and $\gamma = \frac{c_0}{V_m T^3}$. Looks complicated and has lots of coefficients.

Virial function

This is an empirical power series expansion

$$pV_m = A(T) + B(T)p + C(T)p^2 + \dots \tag{11.8}$$

which can alternatively be written as

$$pV_m = A^{'}(T) + \frac{B^{'}(T)}{V_m} + \frac{C^{'}(T)}{V_m^2} + \dots \tag{11.9}$$

where A, B, C and $A^{'}, B^{'}, C^{'}$ are called virial coefficients.

Compressibility factor

For real gases, to clearly display their deviations from ideality we plot the ratio of the observed molar volume, V_m to the ideal gas value as a function of pressure at constant temperature

$$\begin{aligned} Z &= \frac{V_m}{V_{ideal}} \\ &= \frac{V_m}{\frac{RT}{p}} \end{aligned}$$

to obtain

$$\boxed{Z = \frac{pV_m}{RT}}. \tag{11.10}$$

This ratio is called the compressibility factor, Z. Note that for an ideal gas, $Z = 1$. A graph of Z versus pressure will show deviations from 1 indicating non-ideality.

Z, van der Waals gas

Let's calculate Z for the van der Waal gas

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT.$$

Rearrange this to

$$\begin{aligned} \left(p + \frac{a}{V_m^2}\right) &= \frac{RT}{(V_m - b)} \\ p &= \frac{RT}{(V_m - b)} - \frac{a}{V_m^2}. \end{aligned}$$

Now multiply through by V_m

$$pV_m = \frac{RTV_m}{(V_m - b)} - \frac{a}{V_m}.$$

Divide through by RT

$$Z = \frac{pV_m}{RT} = \frac{V_m}{(V_m - b)} - \frac{a}{RTV_m}.$$

The compressibility factor of the van der Waals gas is therefore

$$\boxed{Z = \frac{1}{1-\frac{b}{V_m}} - \frac{a}{RTV_m}} \tag{11.11}$$

This expression can be expressed differently, especially at low pressures where $\frac{b}{V_m} << 1$ by talking a series expansion of the above expression.

The Mclaurin series of $\frac{1}{1-x}$ goes as

$$\frac{1}{1-x} = 1 + x + x^2 + \dots$$

Thus

$$\frac{1}{1-\frac{b}{V_m}} = 1 + \left(\frac{b}{V_m}\right) + \left(\frac{b}{V_m}\right)^2 + \left(\frac{b}{V_m}\right)^3 + \dots$$

Hence

$$Z \simeq 1 + \left(\frac{b}{V_m}\right) + \left(\frac{b}{V_m}\right)^2 + \left(\frac{b}{V_m}\right)^3 - \frac{a}{RTV_m}$$

giving the following equation.

$$\boxed{Z = 1 + \left(b - \frac{a}{RT}\right)\left(\frac{1}{V_m}\right) + \left(\frac{b}{V_m}\right)^2 + \left(\frac{b}{V_m}\right)^3 + \dots} \tag{11.12}$$

Alternatively, it would be preferable to have Z defined as a function of temperature and pressure, but since the van der Waals equation is cubic in V_m this gets complicated fast. We settle for an approximate expression by noting that as the pressure goes to zero ($p \to 0$), $\frac{1}{V_m} \to 0$ and $Z \to 1$ (ideal). Therefore at low pressures we can expand Z as a power series in pressure

$$Z = 1 + A_1 p + A_2 p^2 + A_3 p^3 + \dots$$

where A_1, A_2, A_3 are functions of temperature only. Now to determine A_1, A_2, A_3 note that $Z = \frac{pV_m}{RT}$ (our definition) or that $\frac{1}{V_m} = \frac{p}{RTZ}$. Replace this expression into our volume-based power series expansion

$$\begin{aligned}
Z &= 1 + \left(b - \frac{a}{RT}\right)\left(\frac{1}{V_m}\right) + \left(\frac{b}{V_m}\right)^2 + \left(\frac{b}{V_m}\right)^3 + \dots \\
&= 1 + \left(b - \frac{a}{RT}\right)\left(\frac{p}{RTZ}\right) + \frac{b^2 p^2}{(RTZ)^2} + \frac{b^3 p^3}{(RTZ)^3} + \dots \\
&= 1 + \left(b - \frac{a}{RT}\right)\left(\frac{p}{RTZ}\right) + \left(\frac{b}{RT}\right)^2 \frac{p^2}{Z^2} + \left(\frac{b}{RT}\right)^3 \frac{p^3}{Z^3} + \dots \\
&= 1 + A_1 p + A_2 p^2 + A_3 p^3
\end{aligned}$$

We then have the equality

$$A_1p + A_2p^2 + A_3p^3 + \cdots = \left(b - \frac{a}{RT}\right)\left(\frac{p}{RTZ}\right) + \left(\frac{b}{RT}\right)^2 \frac{p^2}{Z^2} + \left(\frac{b}{RT}\right)^3 \frac{p^3}{Z^3} + \ldots$$

or

$$A_1 + A_2p + A_3p^2 + \cdots = \left(b - \frac{a}{RT}\right)\left(\frac{1}{RTZ}\right) + \left(\frac{b}{RT}\right)^2 \frac{p}{Z^2} + \left(\frac{b}{RT}\right)^3 \frac{p^2}{Z^3} + \ldots$$

By inspection

$$A_1 = \left(b - \frac{a}{RT}\right)\left(\frac{1}{RTZ}\right)$$

and as $Z \to 1$

$$A_1 = \left(b - \frac{a}{RT}\right)\left(\frac{1}{RT}\right)$$

Now we go back and find the other coefficients. We have

$$A_1 + A_2p + A_3p^2 + \cdots = \frac{A_1}{Z} + \left(\frac{b}{RT}\right)^2 \frac{p}{Z^2} + \left(\frac{b}{RT}\right)^3 \frac{p^2}{Z^3} + \ldots$$

Subtract A_1 from both sides and then divide by p to isolate A_2 on the left hand side.

$$\begin{aligned} A_2p + A_3p^2 + \ldots &= \frac{A_1}{Z} - A_1 + \left(\frac{b}{RT}\right)^2 \frac{p}{Z^2} + \left(\frac{b}{RT}\right)^3 \frac{p^2}{Z^3} + \ldots \\ A_2 + A_3p + \ldots &= \frac{A_1}{Z}\left(\frac{1}{p}\right) - \left(\frac{A_1}{p}\right) + \left(\frac{b}{RT}\right)^2 \frac{1}{Z^2} + \left(\frac{b}{RT}\right)^3 \frac{p}{Z^3} + \ldots \end{aligned}$$

From this, by inspection, we see that

$$\begin{aligned} A_2 &= \frac{A_1}{p}\left(\frac{1}{Z} - 1\right) + \left(\frac{b}{RT}\right)^2 \frac{1}{Z^2} \\ &= -\frac{A_1}{p}\left[\frac{Z-1}{Z}\right] + \left(\frac{b}{RT}\right)^2 \frac{1}{Z^2} \\ &= -\frac{A_1}{Z}\left(\frac{Z-1}{p}\right) + \left(\frac{b}{RT}\right)^2 \frac{1}{Z^2} \end{aligned}$$

Since $Z = 1 + A_1 p + A_2 p^2 + \ldots$, $\lim_{p\to 0}\left(\frac{Z-1}{p}\right) = A_1$. Using this we get

$$\begin{aligned} A_2 &= -\frac{A_1}{Z} A_1 + \left(\frac{b}{RT}\right)^2 \frac{1}{Z^2} \\ &= \left(\frac{b}{RT}\right)^2 \frac{1}{Z^2} - \frac{A_1^2}{Z} \end{aligned}$$

Now let $Z = 1$ to get

$$A_2 = \left(\frac{b}{RT}\right)^2 - A_1^2$$

Here we need to evaluate one last thing A_1^2 before we are scott free (who was scott anyway?).

$$\begin{aligned} A_1^2 &= \left(b - \frac{a}{RT}\right)^2 \left(\frac{1}{RT}\right)^2 \\ &= \left[b^2 - \frac{2ab}{RT} + \frac{a^2}{(RT)^2}\right] \left(\frac{1}{RT}\right)^2 \\ &= \left(\frac{b}{RT}\right)^2 - \frac{2ab}{(RT)^3} + \frac{a^2}{(RT)^4} \end{aligned}$$

therefore when this is thrown back into the expression for A_2 we get

$$A_2 = \left(\frac{b}{RT}\right)^2 - \left(\frac{b}{RT}\right)^2 + \frac{2ab}{(RT)^3} - \frac{a^2}{(RT)^4}$$

resulting in

$$A_2 = \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right)$$

This process is repeated on and on to get A_3, A_4 and so forth.

Summary

Expression of the van der Waals gas compressibility ratio expressed as a function of pressure and temperature. Now we can plot this on a Z versus p curve.

$$\boxed{Z(p,T) = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right) p + \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right) p^2 + \ldots} \qquad (11.13)$$

Chapter 12

Equation of state: Condensed phases

At this point, you might be wondering if there is a generic equation of state for condensed phases. In this regard, solids and liquids are referred to collectively as condensed phases. This emphasizes their high density relative to gases. To illustrate, at standard temperature and pressure (STP, this is 0^{o}C or 273.15K and 1 atm) a gas occupies 22,400 cm^3/mol (or 22.4 L) while most solids and liquids occupy between 10 and $100cm^3/mol$. Thus the molar volume of gas is 500-1000 times larger than that of a liquid or a solid. This translates to large differences in the average distance between molecules in the gas phase versus either condensed phase. If the ratio of gas volume to liquid volume is 1000, the ratio of intermolecular distances is roughly

$$\begin{aligned} d^3 &= 1000 \\ d &= \sqrt[3]{1000} = 10. \end{aligned}$$

Molecules in the gas phase are therefore approximately 10 times farther apart than molecules in liquids and especially in solids.

So what really begins to distinguish liquids and solids from gases is the presence of short range intermolecular forces (remember those van der Waals forces for real gases) which fall off very quickly with increasing molecular separation. So in gases, we (for the most part) ignore these intermolecular forces to obtain the ideal gas law. Corrections for reality then lead us to the previous real gas equations of state such as the van der Waals equation, the Berthelot equation etc... As you can probably guess, in condensed phases, these intermolecular forces cannot be ignored.

Again, recall that the three contributions to so-called Van der Waals forces are

- dipole-dipole interactions (Keesom 1912)
- dipole-induced dipole interactions (Debye 1920)
- induced-dipole-induced-dipole interactions (London 1930).

In the absence of orientational averaging, the first dipole-dipole contribution has a $\frac{1}{r^3}$ dependence. After angle averaging, it becomes $\frac{1}{r^6}$. The second dipole-induced dipole term maintains a $\frac{1}{r^3}$ dependence because the second dipole is induced by the first as the name implies. The relative orientation of the dipoles is therefore maintained. The final contribution, induced-dipole-induced-dipole, is shown to possess a $\frac{1}{r^6}$ dependence.

We return to our original question. Is it then possible to find an equation of state for liquids and solids that has the same generality as the ideal gas equation of state? Unfortunately, the answer is no. However, we can develop something that looks like a general equation of state for condensed phases as we will see.

The dependence of the volume of a solid or liquid on temperature at *constant pressure* is

$$\boxed{V(T) = V_0(1 + \alpha T)} \tag{12.1}$$

where V_0 is the volume of a solid or liquid at 0^oC and α is the coefficient of thermal expansion (units of K^{-1}). α is generally the same for all gases but varies dramatically in solids and liquids. This expression is akin to Charles' law in gases. If we wanted to, we can extend this power series to better fit the behavior of a real solid or liquid. So our original expression would change a bit to

$$V(T) = V_0(1 + aT + bT^2 + cT^3 + \dots)$$

where a,b,c,d, etc... are constants. One generally keeps only the first two terms of this expression since the contributions of higher order terms becomes successively smaller.

Now it turns out that V_0 is dependent on pressure just like Boyle's law in gases. Experimentally a relationship between V_0 and pressure is found to be

$$\boxed{V_0(p) = V_0^0[1 - \kappa(p - 1)]} \tag{12.2}$$

at *constant temperature* where V_0^0 is the volume of the condensed phase at 0^oC and at 1 atm, p is the pressure in atm and κ is the coefficient of compressibility with units of atm^{-1}. Note that κ is very small for liquids and solids. They are basically incompressible ($\kappa \simeq 0$). This is why torpedoes are so dangerous to ships.

The above two equations for $V(T)$ and $V(p)$ can be obtained from the definitions of α and κ as illustrated below. Namely, α and κ are formally defined as

$$\boxed{\alpha = \tfrac{1}{V}\left(\tfrac{\partial V}{\partial T}\right)_p} \tag{12.3}$$

$$\boxed{\kappa = -\tfrac{1}{V}\left(\tfrac{\partial V}{\partial p}\right)_T}. \tag{12.4}$$

Derive V(T)

Let's first show how α gives us $V(T) = V_o(1 + \alpha T)$

$$\begin{aligned}
\alpha &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \\
\frac{dV}{V} &= \alpha dT \\
\int_{V_0}^{V} \frac{dV}{V} &= \int_{T_0}^{T} \alpha dT \\
\ln \frac{V}{V_0} &= \alpha(T - T_0) \\
\frac{V}{V_0} &= e^{\alpha(T-T_0)} \\
V = &\ V_0 e^{\alpha(T-T_0)}.
\end{aligned}$$

Now if $\alpha(T - T_0) << 1$ we can express the exponential as a series

$$e^{\alpha(T-T_0)} \simeq 1 + \alpha(T - T_0) + \dots$$

This leads to our first expression for V as a function of T

$$V(T) = V_0[1 + \alpha(T - T_0)] \tag{12.5}$$

where if $T_0 = 0^o$C we obtain the desired original expression.

Derive V(p)

Likewise, we can do the same sort of derivation for $V(p)$

$$\begin{aligned} \frac{dV}{V} &= -\kappa dp \\ \int_{V_0}^{V} \frac{dV}{V} &= -\int_{p_0}^{p} \kappa dp \\ \ln \frac{V}{V_0} &= -\kappa(p - p_0) \\ \frac{V}{V_0} &= e^{-\kappa(p-p_0)}. \end{aligned}$$

Now if $\kappa(p - p_0) << 1$ the exponential can be expressed as a series

$$e^{-\kappa(p-p_0)} \simeq 1 - \kappa(p - p_0) + \ldots$$

resulting in

$$V(p) = V_0[1 - \kappa(p - p_0)]. \tag{12.6}$$

If $p_0 = 1$atm we get our original expression where V becomes V_0 and V_0 becomes V_0^0.

Combining the two

So just like in the ideal gas section where we combined the results of Boyle and Charles (and Avogadro) to get the ideal gas equation let's combine the above two expressions.

$$V(T) = V_0(p)(1 + \alpha T)$$

$$V_0(p) = V_0^0[1 - \kappa(p - 1)].$$

Substituting one equation into the other gives

$$\boxed{V(T,p) = V_0^0[1 - \kappa(p - 1)][1 + \alpha T]}, \tag{12.7}$$

which is a general equation of state for condensed phases. But this result isn't truly as general as the ideal gas equation of state because each solid or liquid has a different V_0^0 and α and κ value. There is no equivalent to the universal ideal gas constant R here.

Chapter 13

First law of thermodynamics

The first law of thermodynamics is basically a statement of the conservation of energy applied to a thermodynamic system of interest. The reason we need the first law is that the systems we will consider ultimately undergo some sort of process, taking it from an initial state to a final state (after all if the system just sat there life would be pretty boring). During these processes, the system exchanges energy with its surroundings and since we don't magically gain or lose energy we need a bookkeeping mechanism to track the changes in internal energy of a system. Obviously, if the system is isolated and just minding its own business, its internal energy will remain the same.

At this point, note three more things. First, we are not specifying exactly what kind of energy the system has gained or lost. Given our knowledge of quantum mechanics, we could say that it's electronic or vibrational or rotational energy gained or lost. But back in the day people didn't know this. Thermo preceded quantum by many years. So in some ways that's the beauty of classical thermodynamics since it applies to everything *irrespective* of what is actually going on inside the system. Next, we are only looking at energy *changes* in thermodynamics. We are not measuring absolute energies of a system. That's the reason for all the deltas and differentials in what follows. Finally, it will be customary to define a system's internal energy in terms of its temperature and volume [$U(T, V)$]. However, it is possible to define a system's internal energy as a function of temperature and pressure. But this is not commonly done though we will show the functional form in the later parts of this chapter for the sake of completeness.

The 1st law of thermodynamics states that the change in internal energy

(U) of a system is

$$\boxed{\Delta U = q + w}. \tag{13.1}$$

You can see that these changes in internal energy occur as a consequence of adding and subtracting heat (q) and work (w) to the system. For infinitesimally small changes in internal energy we write

$$\boxed{dU = dq + dw}. \tag{13.2}$$

Before going on we should make a sign convention clear. **This is important.** If you add energy to the system by doing work on it then w is positive. If the system does some kind of work then w is negative. The same goes with everything else. If the system receives heat, q is positive. If it loses heat during some process then q is negative. I informally call this a selfish "me" perspective. The other analogy is to a checking account you might have at NDFCU. If you add cash to the account the sign is positive. If you use the ATM to withdraw money, the sign is negative. You are warned that there are many texts out there that have an opposite sign convention. So beware!

To continue, we need to describe the kind of work involved here. This is mostly what I will call pressure/volume (PV) work. I will not go into other forms of work other than note that you can have electrical work among other things. Generally speaking we will not deal with these other forms of work here. The heat term is simply the energy transferred to or from the system due to a temperature difference with the surroundings.

Work

Now, when dealing with PV work we are generally dealing with gases and on top of this we are usually dealing with changes in its volume. The work term then looks like

$$\boxed{w = p\Delta V} \tag{13.3}$$

and the internal energy expression becomes

$$\Delta U = q + p\Delta V. \tag{13.4}$$

These volume changes for gases can be large and hence the amount of work done can be significant. Doubt me, then think of the V8 in a car. Everytime you have a volume expansion in one of the cylinders it causes a volume displacement (or displacement, you usually see these written as 1.7 L or 5 L sometimes on the back of the car) by a moving piston which, in turn, enables your car to move. However, if you are dealing with condensed phases like liquids and solids, recall that they are generally incompressible and that any volume changes are almost insignificant. They can be ignored to a first approximation. Basically, $\Delta U \simeq q$ for solids and liquids. As a consequence, in the next section we focus only on gases and not on condensed phases.

Heat transfer

There are three generic heat transfer processes one should be aware of. They are

- Conduction
- Convection
- Radiation

Demo opportunity

Conduction can be demonstrated by heating one end of a metal rod. Wait long enough and the end you are holding will get hot as well. Try holding on to it as long as possible and think of the opening scene in Kung Fu. Alternatively, use a hand boiler filled with methylene chloride. Hold it in your hand and the pressure in the bottom of the bulb will build up. This pressure will then push the liquid up into the top section of the hand boiler.

Convection can be demonstrated using a beaker full of say ethylene glycol. Don't try corn syrup it doesn't work, trust me. Add a few drops of food coloring to the top. I like red. Be careful not to mix it by agitating things. Heat the beaker with an open flame from say a portable stove. As a temperature gradient between the bottom and top of the beaker builds in, you will see the food coloring start to cycle and distribute across the solution. This shows the convection or physical motion of solvent molecules that arises due to a temperature gradient.

Radiation can be demonstrated with a science toy (its called a Crookes radiometer and you can buy these things from companies like Edmund Scientific-problem is as a kid you probably won't appreciate it) that has an evacuated chamber with fan like apparatus on the inside. One side of the blades is painted black. The other side is not painted. When exposed to sunlight, the blades will begin to rotate. You can buy such a toy in most science museum gift shops.

Example

As a warm up example, let's run some numbers. The temperature of 1 mole of substance is raised by heating it with 750 joules of energy. It expands and does the equivalent of 200 J of work. Calculate the change in the system's internal energy.

Ans:

$$\begin{aligned} \Delta U &= q + w \\ &= 750 - 200 \\ &= 550J. \end{aligned}$$

Now, let's look more closely at work done by gases.

Piston example

Think of a car engine piston. A chemical reaction occurs within the cylinder which forms a gas that pushes against the piston head. For simplicity, assume no friction and hence no heat evolved as a direct consequence of the piston moving.

The force acting on the piston can be calculated since

$$\text{pressure} = \frac{\text{force}}{\text{area}}.$$

Now remembering some basic physics

$$\text{force} = (\text{pressure})(\text{area}).$$

So what is the pressure? Well, the pressure is the external pressure (p_{ext}) that the gas inside the piston is pushing against (Remember, we always look at things from the system's point of view). Since the piston is cylindrical, the area is just πr^2. We get

$$\text{force} = (p_{ext})(\pi r^2).$$

At this point, we know that the amount of work done is simply force times distance (assume the z direction as the direction the piston moves in). Furthermore, remember from our sign convention that if the system does work, the sign out front is negative. Thus

$$\begin{aligned} w &= -\text{force}(\text{distance}) \\ dw &= -p_{ext}\pi r^2(dz) \end{aligned}$$

or

$$\boxed{dw = -p_{ext}dV}. \tag{13.5}$$

Integrating then gives

$$\begin{aligned} w &= -\int p_{ext}\pi r^2 dz \\ &= -\int_{V_1}^{V_2} p_{ext}dV. \end{aligned}$$

and yields our desired expression

$$\boxed{w = -\int_{V_1}^{V_2} p_{ext}dV}.$$

Types of work we will encounter

Ok so what next? Let's catalog the types of work you will see often in thermodynamics. Remember again that all of this primarily deals with gases since solids and liquids do little or no PV (i.e pdV) work. Their internal energy changes predominantly through the heat term in the first law.

- A1. isothermal free expansion
- A2. isothermal constant pressure expansion
- A3. isothermal reversible expansion
- B1. adiabatic free expansion
- B2. adiabatic constant pressure expansion
- B3. adiabatic reversible expansion

What distinguishes these different processes is how exactly we carry out the gas expansion (or compression). The keywords you see mean that we impose certain restrictions on the process such as assuming that the system's temperature stays constant or invoking the lack of heat transfer between the system and surroundings in an adiabatic process.

A1. Isothermal (irreversible) free expansion

Assume in this case that the gas inside the piston is pushing against nothing. Picture a vacuum on the other side. Or in science fiction movies think of why people are supposed to blow up if they get sucked out of the spaceship not wearing a space suit. Next, let the expansion against vacuum occur uncontrollably. This expansion is therefore called irreversible. Think of it this way, you never see the guy blown out of the spaceship (or Arnold in Total Recall) subsequently get blown back into the spaceship, do you? The process is therefore not reversible.

Now, in this case $p_{ext} = 0$. Therefore $w = 0$ and no work is done by the system. Finally, something for nothing

$$w = 0.$$

In this irreversible free expansion, the temperature of the gas is not a well defined quantity. It may change during the free expansion. However the temperature quickly returns to equilibrium. **You can therefore consider the free expansion to be effectively isothermal.** (Sometimes problems in certain texts will assume that you know that a free expansion is isothermal.) Furthermore, you recall that in the case of an ideal gas an isothermal process also means that the change in internal energy is zero

$$\Delta U = 0.$$

Then, you also recall that from the first law of thermodynamics if there is no change in internal energy and no PV work, by default there is no heat involved

$$q = 0.$$

Finally, it will be shown later that another thermodynamic state function called enthalpy ($H = U + pV$) also does not change ($\Delta H = 0$) in an ideal gas isothermal process.

To summarize For an isothermal free expansion of an ideal gas

$$\begin{aligned} w &= 0 \\ q &= 0 \\ \Delta U &= 0. \end{aligned}$$

I don't recommend trying to memorize this. Rather I suggest knowing the train of thought that got you to these results.

A2. Isothermal (irreversible) expansion against constant pressure

Ok, this time assume there is no vacuum on the other side so $p_{ext} \neq 0$. Work is therefore done by the system when the gas expands. Using our formula for work

$$w = -\int_{V_1}^{V_2} p_{ext} dV$$

we find

$$w = -p_{ext} \int_{V_1}^{V_2} dV$$

since the external pressure is constant. This integrates to

$$w = -p_{ext}(V_2 - V_1) = -p_{ext}\Delta V$$

which is our desired expression.

Again, note that we have an isothermal expansion. Therefore

$$\Delta U = 0$$

and from the first law of thermodynamics

$$q = -w = p_{ext}\Delta V.$$

Finally, it will be shown later that the change in system enthalpy ($H = u + pV$ or for those who are curious $\Delta H = \Delta U + p\Delta V$) is zero ($\Delta H = 0$).

To summarize For an isothermal constant pressure expansion of an ideal gas

$$\begin{aligned} w &= -p_{ext}\Delta V \\ q &= p_{ext}\Delta V \\ \Delta U &= 0. \end{aligned}$$

Example

To get a numerical feel for this, calculate the work, heat and internal energy change when 1 mole of a gas expands from 5 dm^3 to 10 dm^3 against a constant pressure of 1 atm isothermally.

Ans:

$$\begin{aligned} w &= -p_{ext}(V_2 - V_1) \\ &= -(1atm)(10 - 5dm^3) \end{aligned}$$

where $1atm = 1.01325 \times 10^5 Pa = 1.01325 \times 10^5 \frac{N}{m^2}$ and $1dm = 0.1m$

$$\begin{aligned} w &= -(1.01325 \times 10^5 \frac{N}{m^2})(5)(0.1)^3 m^3 \\ &= -(5 \times 10^5 \frac{N}{m^2})(1 \times 10^{-3}) m^3 \\ &= -(5 \times 10^5 \frac{N}{m^2})(1 \times 10^{-3}) N \cdot m \end{aligned}$$

where $1J = 1N \cdot m$. The desired answer is

$$w = -500J.$$

Note that one can also simplify life if your remember the following unit conversion factor

$$\boxed{1\mathrm{L} \cdot \mathrm{atm} = 101\mathrm{J}}. \qquad (13.6)$$

In this case, you don't have to go through the hassle of multiple unit conversions as done above.

Finally, since the process is isothermal and we are dealing with an ideal gas we can immediately say that $\Delta U = 0$. Again, just accept this fact for now. The exclusive temperature dependence of U for an ideal gas will be shown in the next chapter. Then from the first law of thermodynamics $q = -w$ and $q = 500$ J.

A3. Isothermal (reversible) expansion

This process is pretty common so you should remember it. There are a number of ways to describe this physically but in all cases the idea is that you are doing the expansion infinitely slow. At each point during the expansion you wait long enough so that the system comes to complete equilibrium with the surroundings. This means that at each point of the reversible expansion the system's pressure (p) equals the external pressure (p_{ext}). Recall also that we are assuming an ideal gas. As a consequence, we have

$$p_{ext} = p = \frac{nRT}{V}.$$

We now replace p_{ext} into our work expression and integrate

$$\begin{aligned} w &= -\int_{V_1}^{V_2} p_{ext} dV \\ &= -\int_{V_1}^{V_2} \frac{nRT}{V} dV \\ &= -nRT \int_{V_1}^{V_2} \frac{dV}{V} \\ &= -nRT \ln V|_{V_1}^{V_2} \\ &= -nRT(\ln V_2 - \ln V_1) \end{aligned}$$

or better yet

$$w = -nRT \ln \frac{V_2}{V_1}.$$

It turns out that this reversible work is the maximum work you can extract from the system. At this point, given that the process is isothermal and that we are dealing with an ideal gas ΔU and ΔH are both zero. Finally, from the first law of thermodynamics $q = -w$.

To summarize For the isothermal reversible expansion of an ideal gas

$$\begin{aligned} w &= -nRT \ln \frac{V_2}{V_1} \\ q &= nRT \ln \frac{V_2}{V_1} \\ \Delta U &= 0. \end{aligned}$$

Example

Calculate the amount of work done when 1 mole of a gas expands reversibly from $5dm^3$ to $10dm^3$ at 25^oC.

Ans:

$$\begin{aligned} w &= -nRT \ln \frac{V_2}{V_1} \\ &= -(1mol)(8.314\frac{J}{molK})(298.15K) \ln \frac{10}{5} \end{aligned}$$

The desired result in joules is

$$w = -1718.2J.$$

Adiabatic expansion of an ideal gas

Next, let's talk about the three adiabatic processes mentioned. **By definition, an adiabatic process is one where there is no heat transfer between the system and its surroundings.** Thus no heat gained or lost by the gas in our imaginary piston and from the very start we know that $q = 0$. Next, from the first law of thermodynamics we know then that $\Delta U = w$. These two conclusions are then the conceptual starting point for addressing adiabatic problems.

Now, there are three ways we talked about carrying out an adiabatic expansion

- adiabatic free expansion
- adiabatic (intermediate) constant pressure expansion
- adiabatic reversible expansion

Let's go through them one at a time.

B1. adiabatic free expansion

We start by saying that

$$q = 0$$

since this is an adiabatic process. Next, a free expansion means that $p_{ext} = 0$. As a consequence

$$w = 0.$$

Given the first law of thermodynamics, we finally say that

$$\Delta U = 0$$

It will also be seen later that $\Delta H = 0$.

At this point, take a step back to think about things. Since we are dealing with an ideal gas and since we just found that $\Delta U = 0$ what this is also saying is that the system's temperature didn't change. The expansion was therefore essentially isothermal.

To summarize For the adiabatic free expansion of an ideal gas

$$\begin{aligned} w &= 0 \\ q &= 0 \\ \Delta U &= 0 \\ \Delta T &= 0. \end{aligned}$$

Again, I encourage you to not memorize this. Rather remember the logic that led you to these conclusions.

B2. The adiabatic (intermediate) constant pressure expansion

We again begin by saying that

$$q = 0$$

because the process is adiabatic. The associated work is evaluated using our familiar expression

$$dw = -p_{ext}dV$$

where in the constant external pressure case (the so called intermediate case) you get

$$w = -p_{ext}\Delta V.$$

I want to point out at this stage that there is another equivalent expression for the work involving what is called the constant volume heat capacity. However, let's introduce this in a minute when we begin to discuss the adiabatic reversible expansion of an ideal gas.

From the first law of thermodynamics,

$$\Delta U = -p_{ext}\Delta V.$$

Note that since $\Delta U \neq 0$ and given that we are dealing with an ideal gas, we know that the temperature of the system will change. Our goal in the last part of this chapter will be to determine what exactly the relationship between the initial temperature and final temperature is.

To summarize For the adiabatic constant external pressure expansion of an ideal gas,

$$\begin{aligned} w &= -p_{ext}\Delta V \\ q &= 0 \\ \Delta U &= -p_{ext}\Delta V \\ \Delta T &\neq 0. \end{aligned}$$

B3. The adiabatic reversible expansion

In the reversible case, there will be a complication as you will see when trying to evaluate the work involved in the expansion. First, as always, for an adiabatic process we write

$$q = 0.$$

Then the formula for work is always

$$dw = -p_{ext} dV.$$

So here you say -hmmm, since this is a reversible process $p = p_{ext}$ and since I'm dealing with an ideal gas $p = \frac{nRT}{V}$. Plug this into our expression for work

$$w = -\int \frac{nRT}{V} dV.$$

But here your thermodynamics 6th sense should kick in to alert you that something is wrong. Didn't we just see that in the adiabatic constant external pressure expansion $\Delta T \neq 0$? Maybe ΔT is nonzero in the reversible case. If true, this would mean that we couldn't really integrate our work expression above. In fact, it will be shown that $\Delta T \neq 0$ in the reversible case. As a consequence, we have a problem. To overcome it, just like on a SAT (or GRE) exam, if you don't know the answer to something, keep moving (wait, I must be showing my age. Aren't these exams computerized these days so you can't actually skip questions and come back to them?). Anyway -we move on to calculating the change in internal energy.

Here if you think real deep and remember that $U = f(T, V)$. The total differential is

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV.$$

Next, in an ideal gas, U has no volume dependence (this will be shown through the Joule experiment which will be seen shortly). As a consequence, we are left with

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT.$$

The partial derivative $\left(\frac{\partial U}{\partial T}\right)$ has a name. It is called the constant volume heat capacity (C_V). We will see more of this in the next chapter. For now, assume that C_V is a constant. Thus

$$dU = C_V dT$$

and integrating gives

$$\Delta U = C_V \Delta T.$$

Now, having found both q and ΔU, we use the first law of thermodynamics to obtain the reversible work

$$w = C_V \Delta T.$$

Some things of interest to note at this point. First, for an ideal monatomic gas $C_V = \frac{3}{2}R$. This can be derived from statistical mechanics. Next, note that this C_V-based approach for calculating w can also be applied to the prior adiabatic constant pressure (intermediate) expansion case. However, we didn't need to invoke it since we could readily evaluate w using our normal approach. But as a thought experiment, you might try verifying that both work expressions yield the same answer. Finally, note that we have implicitly assumed that C_V is independent of temperature. This is not formally true. It does have a temperature dependence but in many cases -for a finite temperature range- one can assume that it is constant.

To summarize For the adiabatic reversible expansion of an ideal gas

$$\begin{aligned} w &= C_V \Delta T \\ q &= 0 \\ \Delta U &= C_V \Delta T \\ \Delta T &\neq 0. \end{aligned}$$

Adiabatic processes and temperature changes

But what exactly are the temperature changes involved in w and ΔU above? If we want numbers, we're going to need a more concrete expression for what the temperature change is in an adiabatic expansion (excluding the free adiabatic expansion case). The purpose of the next part of this discussion is therefore to show you that in an adiabatic reversible or intermediate expansion process the final temperature of the system will drop. Conversely, in compression it will rise.

Adiabatic irreversible or intermediate case

Let's begin with the adiabatic constant external pressure expansion process. Note that we assume C_V is independent of temperature which is not always the case but it is a good start.

Since $q = 0$ we have

$$\Delta U = w.$$

This then leads to the following as we have seen

$$\begin{aligned} C_v dT &= -p_{ext} dV \\ \int_{T_1}^{T_2} C_v dT &= -p_{ext} \int_{V_1}^{V_2} dv \\ C_v(T_2 - T_1) &= -p_{ext}(V_2 - V_1) \\ (T_2 - T_1) &= -\frac{p_{ext}}{C_v}(V_2 - V_1) \end{aligned}$$

or

$$\boxed{T_2 = T_1 - \tfrac{p_{ext}}{C_v}(V_2 - V_1)}. \tag{13.7}$$

Provided that $V_2 > V_1$ it's apparent that $T_2 < T_1$. So the gas temperature will drop on expansion and physically this has to do with the system doing work on the surroundings. Conversely, note that the gas will heat on compression. In fact, this is the basis for Diesel engines where the compression stroke of the engine causes the gas in the piston to heat up and ultimately ignite, causing an explosion.

Adiabatic reversible case

Consider now the reversible case where $p_{ext} = p = \frac{nRT}{V}$. Since $q = 0$ we again have

$$\Delta U = w.$$

This becomes

$$\begin{aligned} C_V dT &= -\frac{nRT}{V} dV \\ \frac{C_V dT}{T} &= -\frac{nR}{V} dV \\ C_V \ln \frac{T_2}{T_1} &= -nR \ln \frac{V_2}{V_1} \\ C_V \ln \frac{T_2}{T_1} &= nR \ln \frac{V_1}{V_2}. \end{aligned}$$

Again, remember that we have assumed that C_V does not depend on temperature over the temperature range sampled. Consolidating terms gives

$$\begin{aligned} \ln \frac{T_2}{T_1} &= \frac{nR}{C_V} \ln \frac{V_1}{V_2} \\ \ln \frac{T_2}{T_1} &= \ln \left(\frac{V_1}{V_2} \right)^{\frac{nR}{C_V}} \end{aligned}$$

which can then get rearranged as follows

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\frac{nR}{C_V}}$$

giving

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\frac{nR}{C_V}} .$$

Now, if $V_2 > V_1$ and $nR < C_V$ then $T_2 < T_1$, showing that the gas cools on expansion.

Let's see if this makes any sense. The following table shows you *molar* C_V values and compares it to R where $n = 1$. So this all assumes one mole of gas.

Gas	C_V (J/mol K)	$\frac{C_V}{R}$
Ar	12.5	1.50
He	12.5	1.50
CO	20.7	2.49
H_2	20.4	2.45
HCl	21.4	2.57
N_2	20.6	2.49
NO	20.9	2.51
O_2	21.1	2.54
Cl_2	24.8	2.98
CO_2	28.2	3.40
CS_2	40.9	4.92
H_2S	25.4	3.06
N_2O	28.5	3.42
SO_2	31.3	3.76

Alternatively, it will be shown that for one mole of an ideal gas ($n = 1$) $C_p = C_V + R$ or that $R = C_p - C_V$. Here C_p is called the constant pressure heat capacity. With this, we obtain an equivalent expression for the final temperature T_2. Starting with

$$\ln\frac{T_2}{T_1} = \frac{nR}{C_V}\ln\frac{V_1}{V_2}$$

we have

$$\begin{aligned} \ln\frac{T_2}{T_1} &= \frac{C_p - C_V}{C_V}\ln\frac{V_1}{V_2} \\ &= \left(\frac{C_p}{C_V} - 1\right)\ln\frac{V_1}{V_2} \end{aligned}$$

Now let $\gamma = \frac{C_p}{C_V}$

$$\ln\frac{T_2}{T_1} = (\gamma - 1)\ln\frac{V_1}{V_2}$$

giving

$$\boxed{\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}} \tag{13.8}$$

and since $\gamma > 1$ we see that the final temperature is smaller than the initial $T_2 < T_1$.

Alternatively, we can come up with another equivalent expression using pressures. Since $pV = nRT$

$$\begin{aligned} \frac{T_2}{T_1} &= \frac{p_2 V_2}{p_1 V_1} \\ \left(\frac{V_1}{V_2}\right)\left(\frac{T_2}{T_1}\right) &= \left(\frac{p_2}{p_1}\right) \end{aligned}$$

where from before $\left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}} = \left(\frac{V_1}{V_2}\right)$ so that

$$\begin{aligned} \left(\frac{T_2}{T_1}\right)^{\frac{\gamma-1}{\gamma-1}+\frac{1}{\gamma-1}} &= \left(\frac{p_2}{p_1}\right) \\ \left(\frac{T_2}{T_1}\right)^{\frac{\gamma}{\gamma-1}} &= \left(\frac{p_2}{p_1}\right). \end{aligned}$$

This leaves us with our desired (final) pressure-based expression for the temperature of an ideal gas after an adiabatic reversible expansion

$$\boxed{\left(\frac{T_2}{T_1}\right) = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}}. \tag{13.9}$$

Again, the final temperature will be smaller than the initial temperature. Physically, the system cools a little bit by doing PV (i.e. pdV) work.

In all cases, for a monatomic ideal gas it turns out that (this can be derived using statistical mechanics)

$$\boxed{\gamma = \tfrac{5}{3}} \tag{13.10}$$

$$\boxed{C_V = \tfrac{3}{2}R} \tag{13.11}$$

$$\boxed{C_p = \tfrac{5}{2}R} \tag{13.12}$$

Finally, for the sake of completeness, we can derive an expression that relates the initial and final pressures and volumes. Starting with $pV = nRT$,

$$\begin{aligned} \frac{T_2}{T_1} = \frac{p_2V_2}{p_1V_1} &= \left(\frac{V_1}{V_2}\right)^{\gamma-1} \\ p_2V_2V_2^{\gamma-1} &= p_1V_1V_1^{\gamma-1}. \end{aligned}$$

Here we used the $\frac{T_2}{T_1}$ relationship with volumes. This then results in

$$p_2V_2^{\gamma} = p_1V_1^{\gamma}.$$

Demo opportunity

A demo that one can do is to fire off a fire extinguisher. You will see the carbon dioxide cool during the expansion and will thus see what appears to be snow. Alternatively, one can set off a can of compressed air. Feel the can and you will feel it get cold as the gas is released. Note that an adiabatic compression demo is possible. Namely, you can use a fire syringe that is readily purchased from any science education store. Buy the thick acrylic one though since you're going to slam down hard on the plunger. A glass fire syringe might break.

Put it all together, a thermodynamic cycle

Let's run through an example to put all of these concepts together. One mole of an ideal gas initially at 300K and 1 atm is taken reversibly through a 3 step cycle.

Step 1 The gas expands isothermally until the volume doubles.

Step 2 The gas is then compressed at constant pressure until the original volume is restored

Step 3 The gas undergoes isometric (constant volume) heating until the initial state is reached.

Calculate the work, heat and internal energy change in each step and for the entire cycle. I will do the work for you and presumably you can do the heat and internal energy on your own in your leisure time. Right?

To do this problem, draw a P versus V diagram first. You will notice that we are missing some things, namely V_1, p_2 and T_3. We will therefore need to calculate these values first before proceeding.

What is V_1?

$$\begin{aligned} p_1V_1 &= RT_1 \\ (1)(V_1) &= (0.08206)(300) \end{aligned}$$

We get $V_1 = 24.6L$.

What is p_2? Well we could already say that it's $\frac{1}{2}p_1$ but let's run the numbers for completeness.

$$\begin{aligned} p_2V_2 &= RT_2 \\ p_1V_1 &= RT_1 \end{aligned}$$

where $T_1 = T_2$ and $V_2 = 2V_1$. Plugging these values in we get $p_2 = \frac{1}{2}p_1 = 0.5atm$

What is T_3?

$$\begin{aligned} p_3V_3 &= RT_3 \\ p_2V_2 &= RT_2 \end{aligned}$$

where $p_3 = p_2$ and $V_3 = V_1$ and $V_2 = 2V_1$. Plugging these numbers in we get $T_3 = \frac{1}{2}T_2 = 150K$

What is the work in step 1? This is an isothermal reversible expansion

$$w_1 = -RTln\frac{V_2}{V_1}$$

where $V_2 = 2V_1$. You can run the numbers.

What is the work in step 2? This is a constant pressure compression. Note that the gas cools in this step to maintain its pressure even though its volume decreases.

$$w_2 = -p_{ext}\Delta V$$

where $p_{ext} = p$. We get

$$\begin{aligned} w_2 &= -p(V_1 - 2V_1) \\ &= p_1 V_1. \end{aligned}$$

I'll let you run the numbers.

What is the work in step 3? Easy, $\Delta V = 0$ in an isometric process. No work is done.

$$w_3 = 0.$$

The total work in the cycle is therefore

$$w_{tot} = w_1 + w_2 + w_3$$

You can do ΔU_{tot} and q_{tot} yourselves.

Chapter 14

Heat capacities, internal energy and enthalpy

We just went through a discussion of the 1st law of thermodynamics and the types of work that one typically sees with gases. Recall that solids and liquids are incompressible and hence PV (i.e. pdV) work terms are negligible. Most of the internal energy changes of condensed media therefore result from changes in q. To illustrate, consider the case in the 1st law of thermodynamics where the volume is constant (for a gas, a liquid, or a solid, or whatever)

$$dU = dq + dw.$$

If the volume is strictly constant, then there is no PV work involved in the process whatever it is ($dw = 0$) and we are left with

$$dU = dq.$$

Thus, under constant volume conditions, **the change in heat is the same as the change in internal energy of the system**. This is useful for solids and liquids for evaluating changes in internal energy but not necessarily for gases since PV work can be done.

Now you can see that it would be useful to have a function that relates changes in heat to changes in temperature of the system either at constant volume (this case) or under constant pressure (the next case). Such a function is referred to as the heat capacity. In the most generic of cases, the heat absorbed by a body is found to be proportional to its temperature change

$$q = C(\Delta T).$$

The constant of proportionality is called the heat capacity, C, and is proportional to the mass of the stuff. So the more stuff present the larger C is.

Now there are two versions of the heat capacity that we will encounter. The first is under constant volume conditions. The second is under constant pressure conditions. Hence, the two types of heat capacities are called the constant volume and constant pressure heat capacities (C_V and C_p). Note that they will have different numerical values -especially for gases. But for condensed phases we will find that they will not differ all that much.

Demo opportunity

One can readily demo the mass dependence of C by simply boiling 10 mL of water versus 100 mL. The smaller volume will boil first. So if you have ever asked yourself why a pot of water doesn't boil when cooking spaghetti you can answer the question by suggesting that you have too much water. Reduce it and the pot of water will boil faster.

Since C depends on how much stuff is present (i.e. it is an "extensive" property), we often normalize its value. The normalized heat capacity is therefore called either the molar heat capacity or specific heat capacity. The former is on a per mole basis while the latter is on a per gram basis. The normalized versions of the constant volume heat capacity are

- $C_{V,m}$, the molar heat capacity at constant volume (this is on a per mole basis, J/mol K units)

- c_V, the specific heat capacity at constant volume (this is on a per gram basis, J/g K units)

- $C_{p,m}$, the molar heat capacity at constant pressure (this is on a per mole basis, J/mol K units)

- c_p, the specific heat capacity at constant pressure (this is on a per gram basis, J/g K units)

Note the big C used for the per mole version whereas a small c is used for the per gram version.

At this point, let's rearrange our generic heat capacity expression to emphasize how the temperature of a system changes depending on the value of C

$$\Delta T = \frac{q}{C}.$$

We can see that for a given amount of heat (i.e. energy), the larger C is the smaller ΔT will be. Conversely, the smaller C is the larger temperature jumps one will experience for a given amount of heat added to the system.

Demo opportunity

You can readily show how sensitive temperature changes are to C by carrying out the following experiment. Fill one balloon with air. Fill another with water. The following are the heat capacities of water and air. For the moment, ignore the subscripts.

Material	Molar heat capacity (J/mol K)	Specific heat capacity (J/g K)
H_2O	$C_{v,m} = 74.53$	$c_v = 4.18$
Air	$C_{p,m} = 29.19$	c_p=1.012

This means ignore the different subscripts between the air and water heat capacities. We will show that $C_V \simeq C_p$ for condensed phases shortly.

Now heat the two balloons. You will find that the balloon containing air will get hot faster and will eventually pop. By contrast, the water filled balloon will be ok as long as you don't put a flame directly onto the rubber. Keep it over your laptop as long as you want. You believe in thermodynamics, right? The larger heat capacity of the water absorbs all the energy dumped into the system, preventing the balloon from bursting.

Other demo opportunities that can be pursued include the following:

1. You can boil water over an open flame in a paper cup. The paper will not burn.

2. You can soak a 100 dollar bill in a 50/50 water/ethanol mixture. Light the bill on fire. The bill won't burn.

3. Wrap printer paper around a metal rod tightly. Put the rod over an open flame. The paper will not burn.

Let's continue

The following tables compile the molar and specific heat capacities for various materials to give you a feel for their values. The first table shows heat capacities for some solids and liquids. The second table basically comes from the previous chapter and shows the heat capacities of selected monatomic and polyatomic gases.

Material	Molar heat capacity (J/mol K)	Specific heat capacity (J/g K)
Aluminum	24.3	0.900
Bismuth	25.7	0.123
Copper	24.5	0.386
Gold	25.6	0.126
Lead	26.4	0.128
Silver	24.9	0.233
Tungsten	24.8	0.134
Zinc	25.2	0.387
Mercury	28.3	0.140
Water	75.2	4.186
Ethanol	111	2.4

Gas	C_V (J/mol K)	$\frac{C_V}{R}$
Ar	12.5	1.50
He	12.5	1.50
CO	20.7	2.49
H_2	20.4	2.45
HCl	21.4	2.57
N_2	20.6	2.49
NO	20.9	2.51
O_2	21.1	2.54
Cl_2	24.8	2.98
CO_2	28.2	3.40
CS_2	40.9	4.92
H_2S	25.4	3.06
N_2O	28.5	3.42
SO_2	31.3	3.76

There are some things to notice from these tables. First, an apparent difference exists in the heat capacities of solids, liquids and gases. Classical thermodynamics doesn't really explain these differences -nor does it care. However, one can use a microscopic picture to begin to qualitatively rationalize this trend. Statistical thermodynamics is where a more quantitative basis for these numbers is developed.

In solids, the uptake of energy leads to collective vibrations of component atoms/molecules of the solid. This is what gives it its heat capacity. Though not shown, as the temperature gets smaller and approaches 0K, the solid's heat capacity will approach zero since there isn't enough thermal energy to excite the solid's vibrational modes.

In liquids, there exist additional low frequency vibrational modes that add to the material's ability to absorb energy. **Hence, the overall heat capacity of the liquid will be larger than that of the solid.**

In gases, we lose some of this ability to acquire low energy vibrations of the material since the constituent atoms/molecules are far apart. Heat is then taken up as translational motion which requires significantly larger energies. Hence, the heat capacities of gases will be smaller in general.

In all cases, whether for solids, liquids or gases, increasing the temperature will raise the material's heat capacity since this enables access to more vibrational/translational and rotational modes of the material. Note that we will often assume that the heat capacity is temperature independent when running problems. Obviously, this is not correct but within a limited temperature range it can be a good approximation. Finally, the last table shows that the more atoms a gas has, the larger its heat capacity will be in general. This is because of the many more vibrational modes that such polyatomic systems have relative to their monatomic counterparts.

Internal energy

At this point, recall that we will usually describe the internal energy of a system as a function of T and V. Let's see how U responds to changes in either T or V. We first write the total derivative

$$\boxed{dU = \left(\tfrac{\partial U}{\partial T}\right)_V dT + \left(\tfrac{\partial U}{\partial V}\right)_T dV}. \tag{14.1}$$

It will be seen below that the total differential can ultimately be written as

$$\boxed{dU = C_V dT + \pi_T dV}. \tag{14.2}$$

Ignore for the moment what the various variables are. They are defined below. Let's now consider in detail how U changes.

Changes in U with T under constant volume conditions

Since $dV = 0$ we find from above that

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT.$$

Now, we will define the constant volume heat capacity C_V as follows $C_V = \left(\frac{\partial U}{\partial T}\right)_V$. This gives us

$$dU = C_V dT.$$

On looking at this equation and recalling from our discussion about the relationship between heat and heat capacity -you might guess that dU is related to dq. In fact, they are exactly the same under constant volume conditions. You can see this for yourself very simply as follows. Since under constant volume conditions $dV = 0$ there is no work involved in the process. As a consequence, from the first law of thermodynamics

$$dU = dq$$

and hence **under constant volume conditions heat and internal energy changes are synonymous.** Done.

Changes in U with V under constant temperature conditions

Let's now see how U changes with V under constant T conditions. Starting with the total differential above we see that if $dT = 0$ we are left with

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV.$$

The term in parenthesis is sometimes called the internal pressure (π_T) giving

$$dU = \pi_T dV.$$

It turns out that this internal pressure term is a reflection of non-ideality. We will explicitly show that for an ideal gas $\pi_T = 0$ but for real gases where there are intermolecular interactions such that $\pi_T \neq 0$. In fact,

- $\pi_T = 0$, ideal gas and no interactions between molecule, atoms of the system
- $\pi_T > 0$, real gas, there are *attractive* forces between molecules or atoms of the system
- $\pi_T < 0$, real gas, there are *repulsive* forces between molecules or atoms of the system

Can you rationalize the sign of π_T? For future reference, a table of π_T values would be nice here.

Now, it can be shown (famous annoying words) that

$$\boxed{\pi_T = (\tfrac{\partial U}{\partial V})_T = \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]}. \tag{14.3}$$

This is obtained from (this is another total differential for the internal energy except in terms of entropy and volume. Since we haven't talked about entropy yet, just take my word for it. This is just a preview.)

$$dU = TdS - pdV$$

where using our math skills we can show that

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p.$$

At this point, we will need another expression for $(\frac{\partial S}{\partial V})_T$. We will see later on (i.e. way later) that one can find what it is using the following total differential (one of the four fundamental equations of thermodynamics, again this is a preview)

$$dA = -pdV - SdT$$

where from what are called Maxwell relations

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V.$$

When inserted into our earlier expression for the internal pressure we get our desired expression. The reason why this is desired and more convenient is that using this expression and given an equation of state, one can evaluate what the internal pressure π_T is. For example, try this for the ideal gas and say a van der Waals gas. You can try this on your own in your leisure time. Hopefully, you will find that $\pi_T = 0$ for an ideal gas whereas it is nonzero for a real gas.

Finally, we should mention that for solids and liquids (strictly speaking) $\left(\frac{\partial U}{\partial V}\right)_T \neq 0$. However, since in condensed phases, their densities vary little, $dV \simeq 0$. Hence, we can ignore the volume dependence of their internal energy -even if $\left(\frac{\partial U}{\partial V}\right)_T$ is large.

The Joule experiment

Now, a long time ago Joule went out to try and find out what the value of the internal pressure was for a gas. Joule had two flasks with different volumes. One was evacuated and the other had a gas in it. There was a stopcock separating the two. Joule thought that he could measure π_T by observing the temperature change of the gas when it was allowed to expand into the evacuated container.

When he carried out the experiment, he observed no change in temperature. Joule thus concluded that $\pi_T = 0$. However, it should be noted that he probably didn't have a tremendously sensitive thermometer back then. More recent experiments show that $\pi_T \neq 0$ for real gases. But why did Joule probably feel comfortable with his conclusion? (I'm liberally re-writing history here)

Well, the experiment involved a free expansion. As a consequence, $w = 0$. Next, since he measured no temperature change, $q = 0$ and hence $\Delta U = 0$ by the first law of thermodynamics. Now, we already showed that the total differential for U is

$$dU = C_V dT + \pi_T dV$$

where we just found that $dU = 0$ and $dT = 0$. Given that the volume of the system changed ($dV \neq 0$) it is clear that $\pi_T = 0$ for things to remain self consistent. Hence, there was good reason for Joule to believe that he was right. It turns out that real gases do indeed have a nonzero π_T term. The value is just small and easily overlooked, especially considering the precision of early thermometers. As a minor aside, the Joule experiment is a constant internal energy process. By contrast, you will see shortly that the Joule-Thomson experiment, which is discussed later, is a constant enthalpy process, $\Delta H = 0$

Other dependencies of the internal energy

Here what we want to do is take a step back. We've just seen the dependencies of internal energy with temperature and volume under the constraints of constant temperature and constant volume. But you might be wondering -what about the dependencies of the internal energy as a function of temperature and pressure but now under constant temperature and pressure conditions? Specifically, what are

$$\left(\frac{\partial U}{\partial T}\right)_p$$

$$\left(\frac{\partial U}{\partial p}\right)_T$$

given the total differential of $U = f(T, p)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp.$$

Changes in U with T at constant pressure

Recall, from before that

$$dU = C_V dT + \pi_T dV.$$

Using our math skills, let's rearrange the expression by dividing through by dT and imposing constant p conditions

$$\begin{aligned} \frac{dU}{dT} &= \pi_T \frac{dV}{dT} + C_V \\ \left(\frac{\partial U}{\partial T}\right)_p &= \pi_T \left(\frac{\partial V}{\partial T}\right)_p + C_V. \end{aligned}$$

It turns out that the term $\left(\frac{\partial V}{\partial T}\right)_p$ is basically the coefficient of thermal expansion α ($\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$). We saw this earlier when dealing with the equation of state for condensed phases. We therefore see that $\left(\frac{\partial V}{\partial T}\right)_p = \alpha V$. Putting everything together then gives

$$\boxed{\left(\frac{\partial U}{\partial T}\right)_p = \pi_T \alpha V + C_V} \tag{14.4}$$

and if we have numerical values of α, π_T and C_V for a real gas we can evaluate how its internal energy changes with temperature under constant pressure conditions. In the limit of ideal gases, $\pi_T = 0$ and we find that

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V.$$

Thus, there is no difference between with the temperature dependence of U between constant pressure and constant volume conditions. In general, for real gases things are a little more complicated as you can see.

Changes in U with p under constant temperature conditions

To find this dependency, you again use the same math games you have seen above. I'm going to let you try and figure this out on your own. But I've summarized all these dependencies in the next section. So you can take a peek if you wish to tap out.

Internal energy summary

Since we will be interested in the internal energy changes of a system during a process we summarize what we have learned up to now.

$$\begin{aligned} dU &= dq + dw \\ \Delta U &= q + w \\ dU &= C_V dT + \pi_T dV \\ dU &= q \text{ (constant volume conditions)} \end{aligned}$$

Enthalpy

Constant pressure processes are much more common in chemistry than constant volume processes. Most benchtop reactions occur at 1 atm right? Under constant pressure conditions PV (i.e. pdV) work can be done. Just as in the constant volume case where the change in internal energy equals the heat transfered, there is an analogous relationship that applies in constant pressure situations. But it requires us to define a new state function called the enthalpy, H. **The heat (i.e. energy) gained or lost by a system in a constant pressure process is equal to the change in enthalpy of the system**. Also look at the units of enthalpy. It is something like kJ/mol and simply represents an energy change of the system.

The enthalpy is defined as

$$\boxed{H = U + pV} \tag{14.5}$$

$$\boxed{dH = dq} \tag{14.6}$$

where under constant pressure conditions.

Justification 1

Let's show that the first equation for enthalpy makes sense. From the first law of thermodynamics,

$$dU = dq + dw$$

or

$$dq = dU - dw.$$

Under the following restrictions,

- constant pressure conditions
- $p = p_{ext}$ (i.e. reversible conditions)
- and where we consider only PV work

we find $dw = -pdV$. This gives

$$dq = dU + pdV.$$

Since the pressure is constant, we can add Vdp to the right hand side of the above equation. (basically adding zero)

$$\begin{aligned} dq &= dU + pdV + Vdp \\ &= dU + d(pV) \\ &= d(U + pV). \end{aligned}$$

Thus

$$dq = d(U + pV).$$

The differential heat absorbed/released by the system is therefore the total differential of a new state function, called the enthalpy H. We therefore define the enthalpy as

$$H = U + pV.$$

Justification 2

Next, let's justify the second expression which says that $dH = dq$ under constant pressure conditions. If you think about it, this is identical to the $dU = dq$ criteria under constant volume conditions earlier. Starting with

$$H = U + pV$$

add a small increment to the enthalpy

$$\begin{aligned} (H + dH) &= (U + dU) + (p + dp)(V + dV) \\ H + dH &= U + dU + pV + pdV + Vdp + dpdV. \end{aligned}$$

Now, the last term is small and can be dropped giving

$$\begin{aligned} H + dH &= H + dU + pdV + Vdp \\ dH &= dU + pdV + Vdp. \end{aligned}$$

Recall from the first law that $dU = dq + dw$ so that

$$dH = dq + dw + pdV + Vdp.$$

If the work is carried out reversibly, $p_{ext} = p$ and $dw = -pdV$. Replacing this into our equation gives

$$\begin{aligned} dH &= dq - pdV + pdV + Vdp \\ &= dq + Vdp \end{aligned}$$

and if we operate under constant pressure conditions, $dp = 0$. We obtain

$$dH = dq.$$

Changes in enthalpy, H

Just like with the internal energy, we are primarily concerned with changes in H during a process. We're not interested in an absolute value of H in thermodynamics. So let's summarize here what these ΔH expressions look like. We can then consider the special case of an ideal gas.

First, we will usually define H to be a function of temperature and pressure, $H = f(T, P)$. As a consequence, we write its total differential as

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp.$$

If you are looking for parallels between H and U you will be rewarded since the first term in parenthesis turns out to be the constant pressure heat capacity (C_p). The second term in parenthesis will be a reflection of nonideality and will be related to what is called the Joule-Thompson coefficient. For an ideal gas, the second term is zero just like for the internal energy. Let us discuss this in more detail later.

Next, given the earlier definition of H (i.e. $H = U + pV$) we have

$$\begin{aligned} dH &= dU + d(pV) \\ &= dU + pdV + Vdp \\ \Delta H &= \Delta U + \Delta(pV) \\ &= \Delta U + p\Delta V + V\Delta p \\ &= \Delta U + (p_2V_2 - p_1V_1). \end{aligned}$$

Particular case of an ideal gas

Now, there are simplifications that arise when dealing with an ideal gas. Namely, if $pV = nRT$

$$\begin{aligned}\Delta H &= \Delta U + \Delta(pV) \\ &= \Delta U + \Delta(nRT).\end{aligned}$$

Case 1 If the amount of moles is constant (i.e the system is a pure substance), then we can say

$$\Delta H = \Delta U + nR\Delta T.$$

Case 2 If the amount of moles is changing (e.g. our system is a chemical reaction), and the temperature is constant we can write

$$\Delta H = \Delta U + RT\Delta n.$$

Examples relating ΔH and ΔU

Let's do some examples to demonstrate these relationships. Furthermore, we can compare ΔH to ΔU and see how much of an energy difference exists between the two. What we will find is that, in the case of a gas, the differences between the two can be significant. This is because gases can do pV work through expansion or contraction. **By contrast, condensed phases don't undergo large volume changes and, as a consequence, we will find that $\Delta H \simeq \Delta U$ for liquids and solids.**

Example, Gases

Consider a reaction between ideal gases that leads to a change in the number of moles of gas by one ($\Delta n = 1$). Assume that the process is isothermal. We then have

$$\Delta H = \Delta U + \Delta(pV)$$

which becomes

$$\begin{aligned}\Delta H &= \Delta U + \Delta(nRT) \\ &= \Delta U + RT\Delta n.\end{aligned}$$

For the generation of one mole of an ideal gas at 25^{o}C, the difference between ΔH and ΔU is then

$$\Delta H - \Delta U = (8.315J/molK)(298.15K) = 2.5kJ/mol$$

which is a decently big number. This shows that the ability of gases do pV work makes a big difference in the magnitude of ΔH versus ΔU. By contrast, such differences between enthalpy and internal energy are small when dealing with condensed phases and this is illustrated below in the following two examples.

Example, Condensed phases

The change in internal energy ΔU when 1 mol of $CaCO_3$ in the form of calcite converts to argonite is 21kJ. What is the difference between the enthalpy change and the internal energy change when $p = 1bar$. The respective densities of calcite and argonite are

$$\begin{aligned}\rho_{calcite} &= 2.71\frac{g}{cm^3}\\ \rho_{argonite} &= 2.93\frac{g}{cm^3}\end{aligned}$$

Ans:

$$\begin{aligned}H &= U + pV\\ \Delta H &= \Delta U + \Delta(pV)\\ \Delta H &= \Delta U + p\Delta V + V\Delta p\end{aligned}$$

but since p is constant

$$\Delta H = \Delta U + p\Delta V.$$

For solids and liquids, the change in volume will be tiny. However, for gases the change in volume can be huge. In this case we're dealing with solids.

We need the change in volume which we will get through the densities provided. The molecular weight of $CaCO_3$ is 100 g/mol. As a consequence,

$$\begin{aligned}V_1 &= \frac{100g}{2.71g/cm^3} = 36.9cm^3 = 3.69\times 10^{-5}m^3\\ V_2 &= \frac{100g}{2.93g/cm^3} = 34.1cm^3 = 3.41\times 10^{-5}m^3.\end{aligned}$$

The change in volume from calcite to argonite is therefore

$$\Delta V = -2.8\times 10^{-6}m^3.$$

The change in enthalpy is

$$\begin{aligned}\Delta H &= \Delta U + (1\times 10^5 N/m^2)(-2.8\times 10^{-6}m^3)\\ &= \Delta U - 0.28J\end{aligned}$$

and the difference between the enthalpy and the internal energy is

$$\Delta H - \Delta U = -0.28J.$$

This is a small energy difference. Therefore, the enthalpy is basically the same as the internal energy of a condensed phase ($\Delta H \simeq \Delta U$). This is not true for gases as we have seen earlier.

Example, Condensed phases

Calculate the difference between ΔH and ΔU when 1 mol of grey tin ($\rho = 5.75g/cm^3$) changes to white tin ($\rho = 7.31g/cm^3$) at 10 bar.

Ans:

$$\begin{aligned} H &= U + pV \\ \Delta H &= \Delta U + p\Delta V + V\Delta p \end{aligned}$$

Since the pressure is constant the last term drops out.

$$\Delta H = \Delta U + p\Delta V.$$

Now, we need the change in volume which we will get through the provided densities. The molar weight of tin is 118.7 g/mol. Therefore

$$\begin{aligned} V_1 &= \frac{118.7g}{5.75g/cm^3} = 20.64cm^3 = 2.06 \times 10^{-5}m^3 \\ V_2 &= \frac{118.7g}{7.31g/cm^3} = 16.24cm^3 = 1.62 \times 10^{-5}m^3. \end{aligned}$$

The change in volume is then

$$\Delta V = -4.4 \times 10^{-6}m^3$$

and the change in enthalpy is

$$\Delta H = \Delta U + (1 \times 10^6 N/m^2)(-4.4 \times 10^{-6}m^3).$$

Thus, the difference between enthalpy and internal energy is

$$\Delta H - \Delta U = -4.4J.$$

Again, this is a very small difference, showing that for condensed phases $\Delta H \simeq \Delta U$.

The dependence of H with temperature and pressure, $H = f(T,p)$

We now return to the change in enthalpy as a function of temperature and pressure. Like with internal energy, let's go through each of these changes individually. First, given that $H = f(T,p)$ we write the total differential

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp.$$

We will see below that this total differential can ultimately be written as

$$dH = C_p dT - \mu_{JT} C_p dp.$$

As before don't worry about the variables since they are defined below. Let's go through each dependency separately.

Changes in H with T under constant pressure conditions

At constant pressure, the enthalpy changes with temperature through

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT.$$

Now, we will define the constant pressure heat capacity C_p as follows $C_p = \left(\frac{\partial H}{\partial T}\right)_p$. This gives us

$$dH = C_p dT.$$

On looking at this expression and thinking about our discussion on heat capacities, you might feel tempted to think that dH and dq are related to one other. In fact, they are exactly identical under constant pressure conditions

$$dH = dq.$$

We showed this above. Look to the beginning of this section if you don't believe me.

Changes in H with p under constant temperature conditions

Let's now see how H changes with p under constant temperature conditions. Starting with the total differential above we see that if $dT = 0$ we are left with

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp.$$

The term in parenthesis turns out to be related to the negative product of what is called the Joule-Thompson coefficient (μ_{JT}) with the constant pressure heat capacity. This means we have

$$dU = -\mu_{JT} C_p dp.$$

The Joule-Thompson coefficient is a reflection of non-ideality and we will explicitly show that for an ideal gas $\mu_{JT} = 0$.

Now, it can be shown (again, famous annoying words in any text) that

$$\boxed{\left(\frac{\partial H}{\partial p}\right)_T = \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]}. \tag{14.7}$$

This is a nice expression because you can use an equation of state to find what $\left(\frac{\partial H}{\partial p}\right)_T$ and consequently μ_{JT} actually are.

Our expression is derived from

$$dH = TdS + Vdp$$

which is another one of those total differentials which you haven't been introduced to yet. So just trust me again. Next, using our math skills

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V.$$

At this point, we invoke another total differential (another one of those fundamental equations of thermodynamics)

$$dG = -SdT + Vdp$$

involving what is called the Gibbs free energy. Using a Maxwell relationship, we then find from this that

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

whereupon we can substitute this back into $\left(\frac{\partial H}{\partial p}\right)_T$ to get our desired expression. The reason why this expression is useful is that using it along with an equation of state, one can evaluate what the Joule-Thompson coefficient is since $\left(\frac{\partial H}{\partial p}\right)_T = -\mu_{JT} C_p$. For example, try this for the ideal gas and say a van der Waals gas. You can try this on your own in your leisure time. Hopefully, you will find that $\mu_{JT} = 0$ for an ideal gas whereas it is nonzero for a real gas.

Joule-Thomson experiment

Before going on, note the parallel with the prior U section. This has been deliberate.

Now, many years ago Joule and Thomson carried out an experiment to determine what the Joule-Thompson coefficient of a gas was (obviously I'm rewriting history again). In their experiment, they let a gas expand through a porous plug from a region of constant pressure to another. In our mental picture, the gas flows from the left to the right and the pressure on the left side of the plug is at a higher pressure than the pressure on the right of the plug ($p_1 > p_2$). Apparently the original experiment used a silk handkerchief as the plug. During the process, Joule and Thompson measured the change in temperature that occurred upon expansion of the gas. Their apparatus was insulated so that the expansion process was effectively adiabatic ($q = 0$).

In the experiment, they observed a lower temperature on the low pressure side with the difference in temperature proportional to the difference in pressures. The constant of proportionality is now called the Joule-Thomson coefficient, μ_{JT} and this cooling by adiabatic expansion is called the Joule-Thomson effect. Must be cool to have all sorts of things named after you.

For fun and to show that the Joule-Thomson experiment is a constant enthalpy process, we can model the expansion through two frictionless pistons moving on either side of a porous plug. One piston (the left one) compresses the gas while the other piston (the right one) expands as the gas enters its chamber. This effectively models passing gas from one side of the plug to the other (no -not that kind of gas). The external pressure on the left, p_1 is kept constant as is the smaller external pressure on the right, p_2.

We calculate the work on either side and see what happens. First, the work done *on* the gas on the left during compression under a constant external pressure p_1 is

$$\begin{aligned} w_1 &= -\int_{V_1}^{0} p_1 dV \\ &= p_1 V_1. \end{aligned}$$

In parallel, the work done *by* the gas on the right is

$$\begin{aligned} w_2 &= -\int_{0}^{V_2} p_2 dV \\ &= -p_2 V_2. \end{aligned}$$

The total amount of work done *on* the system is therefore

$$w_{tot} = w_1 + w_2 = p_1 V_1 - p_2 V_2$$

and the total heat absorbed or released *by* the system is 0 since this is an adiabatic process.

$$q_{tot} = 0.$$

From the first law of thermodynamics, the internal energy change is

$$\begin{aligned} \Delta U = U_2 - U_1 &= q_{tot} + w_{tot} \\ U_2 - U_1 &= p_1 V_1 - p_2 V_2. \end{aligned}$$

We find upon rearranging that

$$\begin{aligned} U_2 + p_2 V_2 &= U_1 + p_1 V_1 \\ H_2 &= H_1 \end{aligned}$$

and as a consequence

$$\Delta H = 0.$$

Thus, at the end of the day, the Joule-Thomson experiment is a constant enthalpy process. Compare this to the Joule experiment which is a constant internal energy experiment.

In the Joule-Thompson experiment, Joule and Thomson measured a temperature drop across the porous plug, resulting from cooling of the gas during its expansion. Experimentally then, the value $\left(\frac{\partial T}{\partial p}\right)_H$ is called the Joule-Thomson coefficient, μ_{JT}. How does this relate to $\left(\frac{\partial H}{\partial p}\right)_T$ which is what we were interested earlier when describing the total differential dH? Consider the following cyclic relationship (remember this stuff?)

$$\left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_p = -1.$$

On rearranging things we get

$$\left(\frac{\partial H}{\partial p}\right)_T = -\left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial H}{\partial T}\right)_p$$

whereupon we can identify the first term on the right as the Joule-Thompson coefficient and the second as the constant pressure heat capacity. This yields our desired final relationship

$$\boxed{\left(\frac{\partial H}{\partial p}\right)_T = -\mu_{JT} C_p}, \tag{14.8}$$

which we previously showed equaled to

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p .$$

As a thought problem, you can go and figure out what $\left(\frac{\partial H}{\partial p}\right)_T$ is for a solid or liquid. Hint: $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \beta$, the coefficient of thermal expansion. Consider also the case where β is small.

Special case of an ideal gas

Finally, before going on, let's consider $\left(\frac{\partial H}{\partial p}\right)_T$ for the special case of an ideal gas. Using our earlier expression, you can directly show that this term is zero. Remember it is an expression that reflect nonideality. Here what we want to do is to show an alternate approach for establishing that it is zero.

Start with the definition of H

$$H = U + pV.$$

Since we are dealing with an ideal gas $pV = nRT$

$$H = U + nRT.$$

Next, consider the dependence of H on pressure under constant T conditions

$$\left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial U}{\partial p}\right)_T + \left(\frac{\partial RT}{\partial p}\right)_T .$$

Both terms on the right hand side equal zero yielding

$$\left(\frac{\partial H}{\partial p}\right)_T = 0,$$

which again proves that the enthalpy of an ideal gas depends only on temperature.

By the same token, one can also show that $\left(\frac{\partial H}{\partial V}\right)_T = 0$. We have

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + \left(\frac{\partial RT}{\partial V}\right)_T$$

and it's apparent that both terms on the right equal zero. Again, to reiterate, the enthalpy of an ideal gas depends only on temperature.

Other dependencies of the enthalpy

Here what we want to do is take a step back. We've just seen the dependencies of enthalpy with temperature and pressure under the constraints of constant temperature or constant pressure. But you might be wondering -what about the dependencies of enthalpy as a function of temperature and volume but now under constant temperature and volume conditions? Specifically, what are

$$\left(\frac{\partial H}{\partial T}\right)_V$$
$$\left(\frac{\partial H}{\partial V}\right)_T$$

in the total differential of $H = f(T, V)$

$$dH = \left(\frac{\partial H}{\partial T}\right)_V dT + \left(\frac{\partial H}{\partial V}\right)_T dV.$$

Changes in H with T under constant volume conditions

Like with the earlier U internal energy section, we're going to find this relationship by playing a few math tricks.

Consider the total derivative of $H(p, T)$

$$\begin{aligned} dH &= \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \\ &= C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp. \end{aligned}$$

Rearrange the expression by dividing by dT, keeping the volume constant.

$$\left(\frac{\partial H}{\partial T}\right)_V = C_p + \left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V.$$

Invoke now the Euler chain relation

$$\begin{aligned} \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T &= -1 \\ \left(\frac{\partial p}{\partial T}\right)_V &= -\frac{1}{\left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T}. \end{aligned}$$

Apply the inverter relation so that

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T}.$$

Define $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ as the isothermal compressibility. Also recall that the coefficient of thermal expansion is $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$. Throw these equations back into our Euler-derived expression to get

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\alpha}{\kappa_T}\right).$$

Now, take this and put it back into our original expression for the enthalpy change under constant volume conditions

$$\left(\frac{\partial H}{\partial T}\right)_V = C_p + \left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\alpha}{\kappa_T}\right).$$

At this point, we must change $\left(\frac{\partial H}{\partial p}\right)_T$ to something more recognizable (does this ever end). Let's invoke the Euler chain relationship again.

$$\left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_p = -1.$$

Apply the inverter relationship again

$$\begin{aligned}\left(\frac{\partial H}{\partial p}\right)_T &= -\frac{1}{\left(\frac{\partial p}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_p} \\ &= -\left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial H}{\partial T}\right)_p.\end{aligned}$$

Now define

$$\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H,$$

which is the Joule-Thompson coefficient as seen earlier. Recall also that $\left(\frac{\partial H}{\partial T}\right)_p = C_p$ is the constant pressure heat capacity. Our equation becomes

$$\left(\frac{\partial H}{\partial p}\right)_T = -\mu_{JT} C_p.$$

Finally, replace this back into our original expression for the change in enthalpy with temperature at constant volume to get

$$\left(\frac{\partial H}{\partial T}\right)_V = -\mu_{JT} C_p \left(\frac{\alpha}{\kappa_T}\right) + C_p.$$

The desired final final expression is therefore

$$\boxed{\left(\frac{\partial H}{\partial T}\right)_V = C_p \left(1 - \frac{\mu_{JT}\alpha}{\kappa_T}\right)} \tag{14.9}$$

and describes the change in enthalpy with temperature under constant volume conditions. Note that $\mu_{JT} = 0$ for an ideal gas and just like in the earlier U internal energy section we find that there is no difference between $\left(\frac{\partial H}{\partial T}\right)_V$ and $\left(\frac{\partial H}{\partial T}\right)_p$. They both equal C_p.

Changes in H with V under constant temperature conditions

To find this dependency, you again use the same math games you have seen above. I'm going to let you try and figure this out on your own. But I've summarized all these dependencies in the next section. So you can take a peek if you wish to tap out.

Summary of U and H dependencies

Case 1, U(T,V)

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\boxed{du = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV} \tag{14.10}$$

where $\left(\frac{\partial U}{\partial V}\right)_T$ is measured via the Joule experiment giving π_T, the internal pressure.

Case 2, U(T,p)

$$dU = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp$$

where we found $\left(\frac{\partial U}{\partial T}\right)_p$ earlier. We do it again for completeness and so you don't have to go searching for stuff.

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ \left(\frac{\partial U}{\partial T}\right)_p &= \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \\ &= C_V + \pi_T \left(\frac{\partial V}{\partial T}\right)_p \end{aligned}$$

with $\left(\frac{\partial V}{\partial T}\right)_p$ related to the coefficient of thermal expansion through $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$.

Next, from $U = H - pV$ we get

$$\begin{aligned} \left(\frac{\partial U}{\partial p}\right)_T &= \left(\frac{\partial (H - pV)}{\partial p}\right)_T \\ &= \left(\frac{\partial H}{\partial p}\right)_T - p\left(\frac{\partial V}{\partial p}\right)_T - V\left(\frac{\partial p}{\partial p}\right) \end{aligned}$$

giving

$$\boxed{\left(\frac{\partial U}{\partial p}\right)_T = \left(\frac{\partial H}{\partial p}\right)_T - p\left(\frac{\partial V}{\partial p}\right)_T - V} \qquad (14.11)$$

where $\left(\frac{\partial H}{\partial p}\right)_T = -\mu_{JT} C_p$ and where it was the subject of the Joule-Thomson experiment.

To summarize, we have

$$\boxed{dU = \left[\left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p\right] dT + \left[\left(\frac{\partial H}{\partial p}\right)_T - p\left(\frac{\partial V}{\partial p}\right) - V\right] dp} \qquad (14.12)$$

Case 3, H(T,p)

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

$$\boxed{dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp}$$

where $\left(\frac{\partial H}{\partial p}\right)_T = -\mu_{JT} C_p$ is measured through the Joule-Thomson experiment.

Case 4, H(T,V)

$$dH = \left(\frac{\partial H}{\partial T}\right)_V dT + \left(\frac{\partial H}{\partial V}\right)_T dV$$

where we found $\left(\frac{\partial H}{\partial T}\right)_V$ earlier. We do it again here for the sake of completeness.

$$\begin{aligned}
dH &= \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \\
\left(\frac{\partial H}{\partial T}\right)_V &= \left(\frac{\partial H}{\partial T}\right)_p + \left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V \\
&= C_p + \mu_{JT} C_p \left(\frac{\partial p}{\partial T}\right)_V .
\end{aligned}$$

It can be shown that $\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\alpha}{\kappa}$.

Next,

$$\begin{aligned}
\left(\frac{\partial H}{\partial V}\right)_T &= \left(\frac{\partial (U + pV)}{\partial V}\right)_T \\
&= \left(\frac{\partial U}{\partial V}\right)_T + p\left(\frac{\partial V}{\partial V}\right)_T + V\left(\frac{\partial p}{\partial V}\right)_T
\end{aligned}$$

leaving us with

$$\boxed{\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + p + V\left(\frac{\partial p}{\partial V}\right)_T} \tag{14.13}$$

with $\left(\frac{\partial U}{\partial V}\right)_T = \pi_T$ the subject of the Joule experiment.

To summarize, we have

$$\boxed{dH = \left[\left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V\right] dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p + V\left(\frac{\partial p}{\partial V}\right)_T\right] dV} \tag{14.14}$$

Summary for the particular case of an ideal gas

From the definition of an ideal gas you automatically get

$$\left(\frac{\partial U}{\partial p}\right)_T = 0$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0.$$

Next, what are $\left(\frac{\partial H}{\partial V}\right)_T$ and $\left(\frac{\partial H}{\partial p}\right)_T$?

First one

$$\begin{aligned}\left(\frac{\partial H}{\partial V}\right)_T &= \left(\frac{\partial (U+pV)}{\partial V}\right)_T \\ &= \left(\frac{\partial U}{\partial V}\right)_T + p\left(\frac{\partial V}{\partial V}\right)_T + V\left(\frac{\partial p}{\partial V}\right)_T\end{aligned}$$

giving the general expression

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + p + V\left(\frac{\partial p}{\partial V}\right)_T .$$

Now, if we are dealing with the specific case of an ideal gas we know that $\left(\frac{\partial U}{\partial V}\right)_T = 0$ and $p = \frac{nRT}{V}$ and therefore $\left(\frac{\partial p}{\partial V}\right)_T = -\frac{nRT}{V^2}$. Our original expression reduces to

$$\begin{aligned}\left(\frac{\partial H}{\partial V}\right)_T &= p - \frac{nRT}{V} \\ &= p - p = 0.\end{aligned}$$

Thus

$$\left(\frac{\partial H}{\partial V}\right)_T = 0$$

for an ideal gas.

Second one

$$\begin{aligned}\left(\frac{\partial H}{\partial p}\right)_T &= \left(\frac{\partial (U+pV)}{\partial p}\right)_T \\ &= \left(\frac{\partial U}{\partial p}\right)_T + p\left(\frac{\partial V}{\partial p}\right)_T + V\left(\frac{\partial p}{\partial p}\right)_T\end{aligned}$$

leading to the general expression

$$\left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial U}{\partial p}\right)_T + p\left(\frac{\partial V}{\partial p}\right)_T + V.$$

Now if we are dealing with the specific case of an ideal gas $\left(\frac{\partial U}{\partial p}\right)_T = 0$

$$\left(\frac{\partial H}{\partial p}\right)_T = p\left(\frac{\partial V}{\partial p}\right)_T + V$$

where $V = \frac{nRT}{p}$ gives

$$\begin{aligned}\left(\frac{\partial H}{\partial p}\right)_T &= -\frac{nRT}{p} + V \\ &= -V + V = 0.\end{aligned}$$

We then have the final expression

$$\left(\frac{\partial H}{\partial p}\right)_T = 0$$

for the specific case of an ideal gas.

The relation between C_V and C_p

To end this chapter, is there some relationship between C_V and C_p? The answer is yes, although you might not like how complicated the general case looks. For the specific case of an ideal gas, this simplifies greatly.

Let's go find and find this relationship since we have nothing better to do and because we are curious types like the guy in Moby Dick. Begin with

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

where recall that $H = U + pV$. Therefore, we find that

$$\begin{aligned}dH &= d(U + pV) \\ &= dU + pdV + Vdp.\end{aligned}$$

Since the C_p expression invokes a constant pressure, let's assume constant pressure conditions here

$$dH = dU + pdV.$$

Now, put this back into the C_p expression (the numerator specifically) to get

$$\begin{aligned}C_p &= \left(\frac{\partial H}{\partial T}\right)_p \\ &= \left(\frac{\partial (U + pV)}{\partial T}\right) \\ &= \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p\end{aligned}$$

Note that the first term on the right hand side of the equation is similar to the one we are interested in. Unfortunately it's the change in internal energy at constant pressure, not volume. Close. We've already derived what this expression looks like, but let's do it again for the sake of completeness.

$$\begin{aligned} U &= f(T,V) \\ dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV. \end{aligned}$$

Now, divide by dT and keep the pressure constant

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p.$$

Replace this into the expression for C_p

$$\begin{aligned} C_p &= \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \\ &= \left[\left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p\right] + p\left(\frac{\partial V}{\partial T}\right)_p \\ &= C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p. \end{aligned}$$

We obtain our first expression relating C_p to C_V

$$\boxed{C_p = C_V + \left(\tfrac{\partial V}{\partial T}\right)_p \left[p + \left(\tfrac{\partial U}{\partial V}\right)_T\right]} \tag{14.15}$$

Note that if dV is small $C_p \simeq C_V$ again. This would best apply to condensed phases and **you can therefore remember that for solids and liquids there isn't a huge difference in these two heat capacities**

The special case of an ideal gas

The special case of an ideal gas is simple. Starting with the above result

$$C_p = C_V + \left(\frac{\partial V}{\partial T}\right)_p \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

note that $pV = nRT$ and that $\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p}$. Furthermore, recall that for an ideal gas the internal energy depends only on temperature. Hence $\left(\frac{\partial U}{\partial V}\right)_T = 0$. Putting everything together we get

$$\boxed{C_p = C_V + nR.} \tag{14.16}$$

Nice and simple.

Presumably one could use another gas equation of state, like the van der Waals equation, and get analogous expressions. I'll leave this for you to explore in your leisure time. Furthermore, you can also consider coming up with a qualitative explanation for why C_V and C_p differ.

Alternative expression 1

Let's say that we are masochistic or that we like to play math games. We can express our general result slightly differently. Starting with

$$C_p = C_V + \left(\frac{\partial V}{\partial T}\right)_p \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

the $(\frac{\partial U}{\partial V})_T$ term can be broken down using $U = H - pV$ as follows

$$\begin{aligned}\left(\frac{\partial U}{\partial V}\right)_T &= \left(\frac{\partial(H - pV)}{\partial V}\right)_T \\ &= \left(\frac{\partial H}{\partial V}\right)_T - p - V\left(\frac{\partial p}{\partial V}\right)_T .\end{aligned}$$

Replacing this back into our original C_p expression gives

$$\begin{aligned}C_p &= C_V + \left(\frac{\partial V}{\partial T}\right)_p \left[p + \left(\frac{\partial H}{\partial V}\right)_T - p - V\left(\frac{\partial p}{\partial V}\right)_T\right] \\ &= C_V + \left(\frac{\partial V}{\partial T}\right)_p \left[\left(\frac{\partial H}{\partial V}\right)_T - V\left(\frac{\partial p}{\partial V}\right)_T\right]\end{aligned}$$

where $(\frac{\partial H}{\partial V})_T = \left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T$. This then yields

$$\begin{aligned}C_p &= C_V + \left(\frac{\partial V}{\partial T}\right)_p \left[\left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T - V\left(\frac{\partial p}{\partial V}\right)_T\right] \\ &= C_V + \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T \left[\left(\frac{\partial H}{\partial p}\right)_T - V\right]\end{aligned}$$

where now recall one of our old math relationships $(\frac{\partial V}{\partial T})_p \left(\frac{\partial p}{\partial V}\right)_T = -\left(\frac{\partial p}{\partial T}\right)_V$ to get

$$C_p = C_V - \left(\frac{\partial p}{\partial T}\right)_V \left[\left(\frac{\partial H}{\partial p}\right)_T - V\right].$$

The final alternative version of the relation between C_p and C_V is then

$$\boxed{C_p = C_V + \left(\tfrac{\partial p}{\partial T}\right)_V \left[V - \left(\tfrac{\partial H}{\partial p}\right)_T\right]}. \tag{14.17}$$

Alternative expression 2

Let's say we even have more free time. Alternatively, we can express the above relationship in an even more convoluted way using math gymnastics. Starting with the previous result

$$C_p = C_V + \left(\frac{\partial p}{\partial T}\right)_V \left[V - \left(\frac{\partial H}{\partial p}\right)_T\right]$$

we can modify it by considering H as a function of p and T.

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp.$$

If H is held constant (for those Spanish speaker, ojo!) $dH = 0$.

$$\left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp = 0.$$

Divide by dP to get

$$\left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_H + \left(\frac{\partial H}{\partial p}\right)_T = 0.$$

Therefore

$$\left(\frac{\partial H}{\partial p}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_H .$$

Replace this expression into where we left off with C_p.

$$\begin{aligned}
C_p &= C_V + \left(\frac{\partial p}{\partial T}\right)_V \left[V - \left(\frac{\partial H}{\partial p}\right)_T\right] \\
&= C_V + \left(\frac{\partial p}{\partial T}\right)_V \left[V + \left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_H\right] \\
&= C_V + \left(\frac{\partial p}{\partial T}\right)_V \left[V + C_p \left(\frac{\partial T}{\partial p}\right)_H\right] \\
&= C_V + V\left(\frac{\partial p}{\partial T}\right)_V + C_p \left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial p}{\partial T}\right)_V .
\end{aligned}$$

Consolidate the C_p terms to get

$$C_p\left(1-\left(\frac{\partial T}{\partial p}\right)_H\left(\frac{\partial p}{\partial T}\right)_V\right)=C_V+V\left(\frac{\partial p}{\partial T}\right)_V$$

Our final alternative expression is then (no mas -anyone know what this historical reference is to?)

$$\boxed{C_p=\frac{\left[C_V+V\left(\frac{\partial p}{\partial T}\right)_V\right]}{\left[1-\left(\frac{\partial T}{\partial p}\right)_H\left(\frac{\partial p}{\partial T}\right)_V\right]}}. \tag{14.18}$$

Done.

Chapter 15

Thermochemistry

Previously we primarily dealt with internal energy and enthalpy changes for expansions and other processes of a given substance. In chemistry, however, we often deal with chemical reactions. So the system now isn't a single gas or a single block of something. It's now a reaction consisting of reactants and products. So here we show what the enthalpy change for a process defined as a chemical reaction.

The enthalpy change for a reaction is simply the heat (i.e. energy) absorbed or evolved when a chemical reaction for the breaking and making of chemical bonds occurs at constant pressure and temperature. If you remember your freshman chemistry, processes that result in an evolution of heat are called *exothermic* and have a negative ΔH. Processes that result in the absorption of heat are called *endothermic* and have positive ΔH values. Common examples in real life include self heating drinks and meals as well as single use ice packs. You've seen these at Walgreens I'm sure. These are two easy demos that one can do.

Enthalpy H is a state function. The main consequence of this statement is that the enthalpy change of a reaction is simply the difference in enthalpy between the final and initial states (products minus reactions if you will). The enthalpy changes associated with the formation of any intermediate states does not ultimately matter. However, they can be used in an additive bookkeeping fashion if needed to find the net enthalpy change of a reaction. This principle is called Hess' Law after a Russian chemist named Germain Henri Hess in St. Petersburg. "*The total enthalpy for a reaction is independent of the path by which the reaction occurs.*" Let's illustrate Hess' law using an example. But before we go on, let's make clear some "rules" when dealing with these thermochemical equations.

- When a thermochemical equation is multiplied by any factor, the value of ΔH for the new equation is obtained by multiplying the value of ΔH in the original equation by that value.
- When a thermochemical equation is reversed, the value of ΔH has its sign reversed.
- The enthalpy changes of sub reactions adding up to a net reaction are additive.

Example

Consider the oxidation of carbon monoxide to carbon dioxide at 1 bar, 25^oC.

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$$

The enthalpy change measured during the reaction is $\Delta H = -283kJ$. This is measured through the heat evolved in the reaction because $dH = dq$ for a process at constant pressure. So in practice we have a calorimeter with a known heat capacity. The observed temperature change then gives you the amount of heat involved in the reaction which, in turn, gives you ΔH for the reaction (apart from a sign change).

However, we could have found out this value differently using Hess's Law. Say we measured the enthalpy changes of the two following reactions

$$\begin{aligned} C(\text{graphite}) + \frac{1}{2}O_2 &\rightarrow CO \\ C(\text{graphite}) + O_2 &\rightarrow CO_2 \end{aligned}$$

where the enthalpy change of the first reaction is found to be $\Delta H = -110.5kJ$ and the enthalpy change of the second reaction is found to be $\Delta H = -393.5kJ$. Using these two separate ΔH values, we can calculate the original enthalpy change as follows.

If we reverse the first equation, the sign of the enthalpy change is flipped. If we now add the two reactions together like math equations, we get the net reaction

$$CO + \frac{1}{2}O_2 \rightarrow CO_2.$$

The enthalpy change for this process is then the sum of the two enthalpy changes (the first one being flipped in sign)

$$\begin{aligned} \Delta H_{tot} &= -\Delta H_1 + \Delta H_2 \\ &= 110.5 + (-393.5) = -283kJ. \end{aligned}$$

This is in complete agreement with what was measured directly.

Example

The hydrocarbons ethene and ethane are byproducts from the cracking of oil. The enthalpy change at 25^{o}C for the reaction of graphite and hydrogen gas is 52.26 and -84.68 kJ/mol respectively. Calculate the enthalpy change for the hydrogenation of ethene to give ethane.

Ans: The stated reactions are

$$\begin{aligned} 2C(\text{graphite}) + 2H_2 &\rightarrow C_2H_4 \\ 2C(\text{graphite}) + 3H_2 &\rightarrow C_2H_6. \end{aligned}$$

To use Hess' Law to find the desired reaction

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

take the first equation and flip it. Remember to flip the sign of the enthalpy change as well. We get

$$\begin{aligned} C_2H_4 &\rightarrow 2C + 2H_2 \\ 2C + 3H_2 &\rightarrow C_2H_6. \end{aligned}$$

The net reaction is then the desired one written above (I hope you see this) and the sum of the individual enthalpy changes is

$$\begin{aligned} \Delta H_{tot} &= -\Delta H_1 + \Delta H_2 \\ &= -52.26 + (-84.68) = -136.94kJ. \end{aligned}$$

Example

This example will illustrate why we won't necessarily be using Hess so much. Why? Cause it gets tedious and there is a shorter alternative.

Consider the chemical equation

$$CH_4(g) + 4Cl_2(g) \rightarrow CCl_4(l) + 4HCl(g).$$

What is the net enthalpy change of the reaction when you only have the enthalpy differences for the following reactions (these are provided to you)

$$\begin{aligned} C(\text{graphite}) + 2H_2(g) &\rightarrow CH_4(g)\Delta H_f^o = -74.9kJ/mol \\ C(\text{graphite}) + 2Cl_2(g) &\rightarrow CCl_4(l)\Delta H_f^o = -139kJ/mol \\ \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) &\rightarrow HCl(g)\Delta H_f^o = -92.3kJ/mol. \end{aligned}$$

Note that the subscripts f here stand for the enthalpy of formation. Formation from what? Formation from stuff in their standard states. We will discuss this a little later when we talk about the easier alternative to doing these sorts of problems.

So how do you use these equations to find what you want? Well, let's flip equation 1

$$\begin{aligned} CH_4(g) &\rightarrow C(\text{graphite}) + 2H_2(g)\Delta H_f^o = 74.9kJ \\ C(\text{graphite}) + 2Cl_2(g) &\rightarrow CCl_4(l)\Delta H_f^o = -139.0kJ \\ \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) &\rightarrow HCl(g)\Delta H_f^o = -92.3kJ. \end{aligned}$$

Now what? Multiply equation 3 by four.

$$\begin{aligned} CH_4(g) &\rightarrow C(\text{graphite}) + 2H_2(g)\Delta H_f^o = 74.9kJ \\ C(\text{graphite}) + 2Cl_2(g) &\rightarrow CCl_4(l)\Delta H_f^o = -139.0kJ \\ 2H_2(g) + 2Cl_2(g) &\rightarrow 4HCl(g)\Delta H_f^o = -92.3(4)kJ \end{aligned}$$

Now, add all the equations together. You will notice that the carbons and the hydrogens will cancel. The chlorines will add. We get

$$CH_4(g) + 4Cl_2(g) \rightarrow CCl_4(l) + 4HCl(g)\Delta H_f^o = -433.3kJ.$$

This is our desired answer but we got it by dealing with a bunch of little sub reactions. Imagine if instead of three we had ten or more. It gets ugly fast.

An easier way

Now, there is another way to calculate enthalpy changes using tables. But this requires that we first define some things such as standard conditions. First **the enthalpy change of something in its standard state is zero**. This will be our reference point from which all other enthalpy changes are measured. Note that we are not talking about absolute enthalpies. We're always referring to enthalpy changes. In fact, all of these ΔH values are relative to our more or less arbitrary standard state.

To illustrate, the enthalpy of formation of H_2(g) at 298K, 1 bar is defined to be zero. The same goes for N_2(g) at 298 K and 1 bar. Usually this will be for simple things such as elements or gases. Be careful, though, if the thing is not in its standard state, say H_2(s) or N_2(l) then the associated enthalpy of formation is not zero. This is why you want to pay attention to the state of a substance (i.e. whether it is a solid or a liquid or a gas).

Next, the standard conditions are defined as (note the difference in standard temperature from the earlier definition of STP. This gets annoying when people start playing with reference conditions.)

- standard T, 25^{o}C or 298.15K
- standard p, 1 bar or 1×10^5 Pa
- standard state, pure component at this temperature and pressure

We now define the enthalpy change of a molecule or something else in terms of its standard heat of formation ΔH^o_{298} or ΔH^o_f. Again, you can loosely think of this as the enthalpy associated with a given species but it's really the enthalpy change associated with making it. The superscript means 1 bar pressure. The 298 is obvious. So to summarize ΔH^o_f is the enthalpy change due to 1 mole of a compound being formed under standard conditions from its constituent elements in their standard states.

Example

Calculate the enthalpy change for the gas phase reaction between $H_2(g)$ and $I_2(g)$ at 298K and 1 bar

$$H_2(g) + I_2(g) \rightarrow 2HI(g).$$

Note that $H_2(g)$ is in its standard state. By contrast, $I_2(g)$ is not in its standard state. In fact, the standard state of iodine is a solid ($I_2(s)$). The heat of formation of $HI(g)$ can be looked up in a table and is listed as $\Delta H^o_f = 26.48$ kJ/mol. Before we go on to solve this thing, we must get the heat of formation for iodine

$$I_2(s) \rightarrow I_2(g).$$

Here $I_2(s)$ is in its standard state, the associated heat of formation is zero. Next the heat of formation of $I_2(g)$ is looked up in a table and is $\Delta H^o_f = 62.44$ kJ/mol.

Now, put everything together

$$\begin{aligned} H_2(g) + I_2(g) &\rightarrow 2HI(g) \\ 0 + 62.44 &\rightarrow 2(26.48). \end{aligned}$$

Note that we accounted for the number of moles. The net change in enthalpy is then $\Delta H = -9.48 kJ/mol$. Since this is under constant pressure conditions, the enthalpy change is the amount of heat (i.e. energy) lost to the surroundings, which we basically measure using a calibrated calorimeter and a thermometer.

Example

Calculate the enthalpy of reaction at 25^{o}C for the following reaction

$$3Fe_2O_3(s) + 2NH_3(g) \rightarrow 6FeO(s) + 3H_2O(l) + N_2(g).$$

To do this, we go and look up the standard enthalpies of formation of the different species in a table somewhere. We get (all in units of kJ/mol)

$$\begin{aligned} 3Fe_2O_3(s) + 2NH_3(g) &\rightarrow 6FeO(s) + 3H_2O(l) + N_2(g) \\ 3(-824.2) + 2(-46.1) &\rightarrow 6(-266.3) + 3(-285.8) + 0 \end{aligned}$$

Add up the right, add up the left and take the difference (final minus initial) to get

$$\Delta H_{rxn} = 109.6 kJ.$$

So this is trivial. Cake. I'll claim that it is one of the more straightforward aspects of this class. You just have to remember

$$\text{Final} - \text{Initial},$$

taking into account the stoichiometry of the reaction. You also need to look up the standard enthalpies of formation of the different reactants and products in a table. The thing you have to be aware of is that when you do this you are evaluating ΔH for given conditions, namely 25^oC and 1 bar.

Variation of enthalpy with temperature

Ok, so not all reactions are run at 25^{o}C right? How do we calculate the enthalpy change if the reaction occurs at a different temperature? Well, we have to consider the temperature dependence of H under constant pressure conditions. This brings us back to our friend the constant pressure heat capacity, C_p

$$\begin{aligned} C_p &= \left(\frac{\partial H}{\partial T}\right)_p \\ dH &= C_p dT \\ \int dH &= \int_{T_1=298.15}^{T_2} C_p dT. \end{aligned}$$

This last equation is called Kirchoff's Equation (not to be confused with Kirchoff's Law in electrical engineering, besides are these guys related?).

Now Kirchoff's equation would appear to be a straightforward integral. However, C_p actually varies with temperature and is not necessarily constant. We glossed over this when we first talked about heat capacities. So to make life easy, to a first approximation, you can assume that C_p is constant or you can use the average value of the heat capacity $\bar{C_p}$ over the desired temperature range. If you ever saw the movie Heartbreak Ridge with Clint Eastwood, this is an example of what I call improvising, adapting and overcoming). But we almost overlooked something, this average heat capacity must be known for each species in the reaction. So if you have a table that lists them then great, otherwise you have to assume that the heat capacities are all constant with temperature.

At this point, we have

$$\begin{aligned} \Delta H &= \bar{C_p}\Delta T \\ \Delta H_{T_2} - \Delta H_{T_1} &= \bar{C_p}(T_2 - 298.15K) \end{aligned}$$

or

$$\boxed{\Delta H_{T_2} = \Delta H_{T_1} + \bar{C_p}(T_2 - 298.15K)} \qquad (15.1)$$

Here I'm just writing out ΔH explicitly for the final and initial states to remind you that we are not dealing with absolute enthalpies but rather enthalpy changes.

This expression applies to each species in the reaction. Note that an easy way to calculate the change in enthalpy of a reaction at a different temperature is to first calculate the net change of enthalpy like usual. Then go and find the heat capacities or average heat capacities of each species and treat them the same way. Get the net heat capacity of the reaction by adding up the left, adding up the right, taking into account the stoichiometry (remember C depends on how much stuff you have) and taking the difference, final minus initial. This will give you $C_p(net)$ or $\bar{C_p}(net)$ which you would multiply by the temperature difference and add to the 25^{o}C enthalpy change to get the final answer.

Example

The complete combustion of ethane releases 1558.8 kJ of energy at 25^{o}C. Calculate $\Delta H_{combustion}$ at 100^{o}C.

$$C_2H_6(g) + \frac{3}{2}O_2(g) \quad \rightarrow \quad 2CO_2(g) + 3H_2O(l)$$

Given are (all units are in J/mol K)

- $\bar{C_p}(C_2H_6)(g) = 52.6$
- $\bar{C_p}(O_2)(g) = 29.5$
- $\bar{C_p}(CO_2)(g) = 37.1$
- $\bar{C_p}(H_2O)(l) = 75.3$

Ans: Using Kirchoff's equation we get

$$\begin{aligned} \Delta H_{373.15} &= \Delta H_{298.15} + \bar{C_p}(373.15 - 298.15) \\ &= -1558.8 + \bar{C_p}(373.15 - 298.15) \\ &= -1558.8 + \bar{C_p}(75) \end{aligned}$$

where we find $\bar{C_p}(net)$ as follows

$$\begin{aligned} C_2H_6 + \frac{3}{2}O_2(g) &\quad \rightarrow \quad 2CO_2 + 3H_2O \\ 52.6 + \frac{3}{2}(29.4) &\quad \rightarrow \quad 2(37.1) + 3(75.3). \end{aligned}$$

Add up the left, add up the right, take their difference to get $\bar{C_p} = 203.4J/K$. Replace this back into our expression for the enthalpy.

$$\Delta H_{T_2} = -1558.8(1000) + \left(\frac{203.4}{1000}\right)(75) = -1543.5kJ.$$

A more accurate treatment of heat capacity

We know that C_p can change with temperature. In fact, C_p can change significantly in some cases. The variation of C_p with temperature is usually represented as a power series in temperature

$$C_p(T) = a + bT + cT^2 + dT^3 + \dots$$

where one keeps as many terms as necessary to make it an accurate representation of what happens in real life. The coefficients a, b, and c etc... are empirically determined.

Let's consider the specific case where only the first 3 terms in the series are needed. We get for the temperature dependence of the enthalpy

$$\begin{aligned} dH &= C_p dT \\ dH &\simeq (a + bT + cT^2)dT \\ \Delta H &\simeq \int_{T_1}^{T_2} a + bT + cT^2 dT \\ &\simeq a(T_2 - T_1) + \left.\frac{bT^2}{2}\right|_{T_1}^{T_2} + \left.\frac{cT^3}{3}\right|_{T_1}^{T_2}. \end{aligned}$$

The final answer for the change in enthalpy due to a temperature change is therefore

$$\Delta H \simeq a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3).$$

Example

Given the standard enthalpy of formation and heat capacity data below, calculate the enthalpy change at 100^{o}C.

$$3C_2H_2 \rightarrow C_6H_6$$

- $\Delta H_f^o(C_2H_2) = 226.7 kJ/mol$
- $\Delta H_f^o(C_6H_6) = 82.9 kJ/mol$
- $C_p(C_2H_2) = 30.7 + 5.28 \times 10^{-2}T - 1.63 \times 10^{-5}T^2 J/molK$
- $C_p(C_6H_6) = -1.7 + 32.5 \times 10^{-2}T - 11.06 \times 10^{-5}T^2 J/molK$

Ans: We need to find what $\bar{C_p}(net)$ is first. Then we can use it in Kirchoff's expression.

$$\begin{aligned}
\bar{C_p}(net) &= -1.7 + 32.5\times10^{-2}T - 11.06\times10^{-5}T^2 \\
&- 3(30.7 + 5.28\times10^{-2}T - 1.63\times10^{-5}T^2) \\
&= -1.7 + 32.5\times10^{-2}T - 11.06\times10^{-5}T^2 \\
&- 92.1 - 15.85\times10^{-2}T + 4.89\times10^{-5}T^2 \\
&= -93.8 + 16.66\times10^{-2}T - 6.17\times10^{-5}T^2 \text{ J/K}
\end{aligned}$$

Put this back into Kirchoff's expression

$$\begin{aligned}
\Delta H^o_{373} &= \Delta H^o_f + \int_{T_1}^{T_2} -93.8 + 16.66\times10^{-2}T - 6.17\times10^{-5}T^2 dT \\
&= \Delta H^o_f - 93.8(T_2 - T_1) + \frac{16.66\times10^{-2}}{2}(T_2^2 - T_1^2) - \frac{6.17\times10^{-5}}{3}(T_2^3 - T_1^3) \\
&= \Delta H^o_f - 3.365kJ \\
&= -597.2kJ - 3.365kJ \\
&= -600kJ.
\end{aligned}$$

This is our desired answer.

Enthalpy changes for other processes

There are other important enthalpy changes that we should be aware of. They are listed below along with a little blurb. Think of them like the name reactions in second semester organic chemistry. Remember the Cannizzaro reaction?

Enthalpy of combustion, (aka heat of combustion)

This is the enthalpy change when 1 mol of a compound reacts completely with excess O_2. For example,

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l).$$

Tables of these ΔH_{comb} values exist.

Bond dissociation enthalpy, (aka bond energies)

This represents the energy/mol needed to break a chemical bond. For example,

$$CH_4(g) \rightarrow C(g) + 4H(g).$$

Tables of these ΔH_{bond} values also exist.

Example

Use values of bond energies to estimate the standard enthalpy change for the reaction

$$CH_3OCH_3(g) \rightarrow C_2H_5OH(g)$$

Given:

- $\Delta H(C-H) = 415kJ/mol$
- $\Delta H(C-O) = 350kJ/mol$
- $\Delta H(C-C) = 348kJ/mol$
- $\Delta H(O-H) = 464kJ/mol$

Note the sign, these are the energies needed to blow up the bond. It takes energy inputted into the system to blow a bond up. Conversely, if you make a bond you have to flip the sign. This shows how the system stabilizes on bond formation.

On the left side of our reaction, we need to calculate the total energy needed to blow up all bonds.

$$\begin{aligned} \Delta H_1 &= 6(C-H) + 2(C-O) \\ &= 6(415) + 2(350) = 3190kJ. \end{aligned}$$

On the right side of the reaction, we need to calculate the total energy change which results from forming the molecule

$$\begin{aligned} \Delta H_2 &= -[5(C-H) + (C-C) + (C-O) + (O-H)] \\ &= -[5(415) + (348) + (350) + (464)] \\ &= -3237kJ. \end{aligned}$$

Now put everything together by summing the two enthalpy changes, the first to blow up the reactants and the second to form the products

$$\Delta H_{net} = \Delta H_1 + \Delta H_2 = -47kJ.$$

Enthalpy of solution

This is the enthalpy change when 1 mol of a compound dissolves in a large excess of a pure solvent. For example

$$HCl(g) + H_2O(\text{excess}) \rightarrow HCl(aq).$$

Enthalpies associated with phase changes

Fusion

This is the transition from $s \rightarrow l$. ΔH_{fus} (the enthalpy of fusion, aka the latent heat of fusion) is the energy required at constant pressure to melt 1 mol of a pure substance at its melting point, T_m.

Vaporization

This is the transition from $l \rightarrow g$. ΔH_{vap} is the energy required at constant pressure to vaporize 1 mol of a pure liquid at its boiling point, T_b.

Sublimation

This is the transition from $s \rightarrow g$. Think of dry ice where we skip the liquid phase. So ΔH_{sub} is the energy required to take 1 mole of a substance from solid to gas at its sublimation temperature, T_{sub} under constant pressure conditions. Note that enthalpy is a state function. As a consequence,

$$\boxed{\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}}. \tag{15.2}$$

This is a direct application of Hess's Law at constant temperature.

Chapter 16

Entropy and the 2nd and 3rd Laws of Thermodynamics

The purpose of this section is to explain the origin of spontaneity of physical and chemical processes. Namely, you might have gotten the impression from prior classes that spontaneous reactions or processes are those which are exothermic. But what really drives reactions? Let's look at two spontaneous reactions.

The first involves dissolving a salt in water.

$$\mathrm{LiCl~(s)} \rightleftharpoons \mathrm{Li^+(aq)} + \mathrm{Cl^-(aq)}.$$

This process has an enthalpy change of $\Delta H = -37.1$ kJ. It is exothermic.

The next spontaneous process also involves dissolving a salt in water.

$$\mathrm{NaCl~(s)} \rightleftharpoons \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)}.$$

This process has an enthalpy change of $\Delta H = 3.9$ kJ. It is endothermic. Yet it is spontaneous. To drive home this point even more, consider the following spontaneous reaction involving the melting of ice at room temperature

$$\mathrm{H_2O~(s)} \rightleftharpoons \mathrm{H_2O~(l)}.$$

The enthalpy change here is $\Delta H = 6kJ$. Again, here is an endothermic process which we know beyond all doubt is spontaneous. So we conclude that the spontaneity of reactions is not always controlled by favorable final/initial state energy differences. Instead, is there something that is more predictive as to whether a process or reaction is spontaneous?

To better predict spontaneity, we therefore introduce a new thermodynamic function called entropy (S). It is defined as

$$\boxed{dS = \frac{dq_{rev}}{T}} \tag{16.1}$$

where q_{rev} is the heat released or absorbed during a **reversible** process. The unit of entropy is J/mol K. Qualitatively, entropy is a measure of the randomness or disorder of the system. The main idea then is that spontaneous processes are those which tend to increase disorder in the system although we will see a more encompassing definition of spontaneity when we encounter the second law of thermodynamics in a minute. Now, the statistical definition of entropy is

$$\boxed{S = k_B lnW}. \tag{16.2}$$

This relationship was derived by Boltzmann and is written on his tombstone in Vienna. In the expression, k_B is called the Boltzmann constant ($k_B = 1.38 \times 10^{-23}$J/K. It can be found from R/N_A) and the W is basically the number of ways in which you can arrange the molecules in a system.

Uses of entropy to show you're part of the intelligentsia

Clean up your room.

Ans: "Why bother, it's entropically unfavorable"

How come it's such an ordeal get organized to leave for the Linebacker on time?

Ans: "Clearly it's against the Second Law"

etc... you get the point.

Second Law of Thermodynamics

Entropy is key to the second law of thermodynamics. The second law is stated a number of ways but all with the same intent. "*The entropy of an isolated system increases in the course of a spontaneous change*" or "*Spontaneous process are those which increase the entropy of the universe*". So what this is saying is that if we learn how to quantify changes in entropy, we can, predict whether a process is spontaneous or not.

Note that Clausius has another statement of the second law (we'll stick with the top ones, but they're all saying the same thing again). "*It is impossible to construct a machine that is able to convey heat by a cyclical* *process from one reservoir to another at a higher temperature unless work is done on the machine by some outside agency.*" This statement is basically saying that we cannot construct a perpetual motion machine. Note that there are two types of perpetual motion machines, a) those that violate the 1st law of thermodynamics and b) those that violate the 2nd law of thermodynamics.

Note also that thermodynamics has never ever been proven wrong, thus everytime you see someone claiming one of these something for nothing gimmicks (free energy for all) it's probably not true (this also assumes that you're not one of those conspiracy theory people who believe the military-industrial complex is suppressing the release of these free energy machines to continue our dependency on crude oil).

Entropy change preface

Let's see how the entropy of a system might change with temperature and pressure, $S(T, p)$, or temperature and volume, $S(T, V)$. First some preliminaries.

The internal energy of a system is defined as

$$dU = dq + dw.$$

If only pV work is done and the process is done reversibly

$$dU = dq_{rev} - pdV$$

thus

$$dq_{rev} = dU + pdV.$$

The entropy change of the process is then

$$\begin{aligned} dS &= \frac{dq_{rev}}{T} \\ &= \frac{dU + pdV}{T}. \end{aligned}$$

This gives an expression for $S(U, V)$

$$\boxed{dS = \tfrac{1}{T}dU + \tfrac{p}{T}dV} \qquad (16.3)$$

which relates changes in entropy to changes in energy and volume under a given pressure and temperature.

Note the following

- (a) At constant volume ($dV = 0$) an increase in the internal energy of the system means that the entropy increases. Kinda makes sense, yes?
- (b) If the internal energy is constant, an increase in volume implies an increase in entropy.

Now, we do not normally control the energy of a system directly. Pressure and temperature or volume and temperature are more convenient parameters to vary. We therefore convert our original expression to more useful forms.

Variations of entropy with temperature and volume, $S(T, V)$

Consider entropy as a function of temperature and volume $S(T, V)$. The total differential is

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV.$$

A priori who knows what $\left(\frac{\partial S}{\partial T}\right)_V$ and $\left(\frac{\partial S}{\partial V}\right)_T$ are. Well, we can find them by referring to our previous relation for $S(U, V)$.

Compare the above to our previously derived expression

$$dS = \frac{1}{T}dU + \frac{p}{T}dV.$$

Let's work with this second expression and get rid of dU. Do this by expressing the total differential for $U(T, V)$

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ &= C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \end{aligned}$$

where recall $\left(\frac{\partial U}{\partial V}\right)_T = \pi_T$ (the internal pressure)

Use this value of dU in our previous expression for the entropy.

$$\begin{aligned} dS &= \frac{1}{T}\left[C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV\right] + \frac{p}{T}dV \\ &= \frac{C_V}{T}dT + \frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T dV + \frac{p}{T}dV \\ &= \frac{C_V}{T}dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV. \end{aligned}$$

Now, by comparing this to the total differential for the entropy as a function of T and V, shown at the beginning of this section

$$\boxed{\left(\tfrac{\partial S}{\partial T}\right)_V = \tfrac{C_V}{T}} \tag{16.4}$$

$$\boxed{\left(\tfrac{\partial S}{\partial V}\right)_T = \tfrac{1}{T}\left[\left(\tfrac{\partial U}{\partial V}\right)_T + p\right]} \tag{16.5}$$

where from our prior work on the p/V dependencies of internal energy

$$\left(\frac{\partial U}{\partial V}\right)_T = \pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p.$$

The first expression describes the fact that at constant volume the entropy will increase with temperature. The second expression, the volume dependence at constant temperature, is more complicated. We will evaluate this and reduce it to something more tractable. Namely, we will use the exactness of a total differential to help us here. Recall that this meant that the cross derivatives equaled. Note that you could just as well evaluate this by shoving in the explicit form of $\left(\frac{\partial U}{\partial V}\right)_T$ into our expression for $\left(\frac{\partial S}{\partial V}\right)_T$. It will simplify greatly and you find that $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$. But let's demonstrate this another way in what follows.

We start with the exactness relationship

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V}.$$

Left hand side. The left hand side of the expression simplifies as follows

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial}{\partial V}\left(\frac{C_V}{T}\right)$$

where recall that $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

$$\begin{aligned}\frac{\partial^2 S}{\partial V \partial T} &= \frac{\partial}{\partial V}\left[\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V\right] \\ &= \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T}.\end{aligned}$$

We therefore have

$$\left(\frac{\partial^2 S}{\partial V \partial T}\right) = \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T}.$$

Next, the right hand side We have

$$\begin{aligned}
\frac{\partial^2 S}{\partial T \partial V} &= \frac{\partial}{\partial T}\left[\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\right] \\
&= \frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T + \frac{p}{T}\right] \\
&= \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{-1}{T^2}\right) + \frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_V - \frac{p}{T^2}.
\end{aligned}$$

The resulting expression is

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{1}{T}\left[\frac{\partial^2 U}{\partial T \partial V} + \left(\frac{\partial p}{\partial T}\right)_V\right] - \frac{1}{T^2}\left[p + \left(\frac{\partial U}{\partial V}\right)_T\right].$$

Now equate the left and right hand side expressions.

$$\begin{aligned}
\frac{\partial^2 S}{\partial V \partial T} &= \frac{\partial^2 S}{\partial T \partial V} \\
\frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} &= \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} + \frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_V - \frac{1}{T^2}\left[p + \left(\frac{\partial U}{\partial V}\right)_T\right].
\end{aligned}$$

The first two terms cancel because U is a state function and its differential will be exact. This leaves

$$\begin{aligned}
\frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_V &= \frac{1}{T^2}\left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] \\
\left(\frac{\partial p}{\partial T}\right)_V &= \frac{1}{T}\left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]
\end{aligned}$$

and on comparing this result with our original expression for the entropy change with volume under constant temperature conditions

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

we conclude that

$$\boxed{\left(\tfrac{\partial S}{\partial V}\right)_T = \left(\tfrac{\partial p}{\partial T}\right)_V}. \tag{16.6}$$

Thus $\left(\frac{\partial S}{\partial V}\right)_T$ reduces to something more tractable in terms of the coefficient of thermal expansion α and the coefficient of compressibility κ. Recall that

$$\begin{aligned}
\alpha &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \\
\kappa &= -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T
\end{aligned}$$

so that

$$\begin{aligned}\left(\frac{\partial V}{\partial T}\right)_p &= \alpha V \\ \left(\frac{\partial V}{\partial p}\right)_T &= -\kappa V\end{aligned}$$

and by the Euler Chain relation/inverter

$$\begin{aligned}\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T &= -1 \\ \left(\frac{\partial p}{\partial T}\right)_V &= -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T \\ \left(\frac{\partial p}{\partial T}\right)_V &= -(\alpha V)\left(-\frac{1}{\kappa V}\right) \\ &= \frac{\alpha}{\kappa}.\end{aligned}$$

Hence

$$\boxed{\left(\tfrac{\partial S}{\partial V}\right)_T = \left(\tfrac{\partial p}{\partial T}\right)_V = \tfrac{\alpha}{\kappa}}. \tag{16.7}$$

Now putting everything together we find

$$\begin{aligned}dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \\ \boxed{dS = \tfrac{C_V}{T} dT + \tfrac{\alpha}{\kappa} dV}.\end{aligned} \tag{16.8}$$

This expression is applicable to any substance. Except for gases, the volume dependence is usually negligible. Thus for solids and liquids $dS \simeq \frac{C_V dT}{T}$.

Variations of entropy with temperature and pressure, $S(T,p)$

Alternatively, consider the entropy as a function of temperature and pressure $S(T,p)$. The total differential is

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp.$$

Again we don't know a priori what $\left(\frac{\partial S}{\partial T}\right)_p$ and $\left(\frac{\partial S}{\partial p}\right)_T$ are.

But from before (the preface) we found that

$$dS = \frac{1}{T}dU + \frac{p}{T}dV.$$

To simplify this latter expression and to allow an evaluation of $\left(\frac{\partial S}{\partial T}\right)_p$ and $\left(\frac{\partial S}{\partial p}\right)_T$ we introduce the relation $H = U + pV$ or better yet $U = H - pV$. From this we get $dU = dH - pdV - Vdp$. Replace this into our entropy expression above.

$$\begin{aligned} dS &= \frac{1}{T}[dH - pdV - Vdp] + \frac{p}{T}dV \\ &= \frac{1}{T}dH - \frac{p}{T}dV - \frac{V}{T}dp + \frac{p}{T}dV \end{aligned}$$

$$\boxed{dS = \tfrac{1}{T}dH - \tfrac{V}{T}dp.}$$

Obviously, we need to get rid of dH, otherwise what we just did wasn't that useful. Consider $H(T,p)$. The total differential is

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp.$$

Replace this into the previous dS expression to get

$$\begin{aligned} dS &= \frac{1}{T}\left[\left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp\right] - \frac{V}{T}dp \\ &= \frac{1}{T}C_p dT + \frac{1}{T}\left(\frac{\partial H}{\partial p}\right)_T dp - \frac{V}{T}dp \\ &= \frac{C_p}{T}dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial p}\right)_T - V\right] dp. \end{aligned}$$

Now by comparison with the original entropy total differential at the beginning of this section

$$\boxed{\left(\tfrac{\partial S}{\partial T}\right)_p = \tfrac{C_p}{T}} \tag{16.9}$$

$$\boxed{\left(\tfrac{\partial S}{\partial p}\right)_T = \tfrac{1}{T}\left[\left(\tfrac{\partial H}{\partial p}\right)_T - V\right]}. \tag{16.10}$$

Note that $\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$, which we learned in the previous chapter. However, let's show this another way to illustrate that there are many ways to skin a cat (how did this colloquialism get started anyway?). Simplify the second expression just like we did earlier by taking advantage of exactness. We know that

$$\frac{\partial^2 S}{\partial p \partial T} = \frac{\partial^2 S}{\partial T \partial p}$$

The left hand side

$$\frac{\partial}{\partial p}\left(\frac{\partial S}{\partial T}\right)_p = \frac{\partial}{\partial p}\left(\frac{C_p}{T}\right)$$

where $C_p = \left(\frac{\partial H}{\partial T}\right)_p$ so that

$$\begin{aligned}\frac{\partial}{\partial p}\left(\frac{\partial S}{\partial T}\right)_p &= \frac{\partial}{\partial p}\left[\frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_p\right] \\ &= \frac{1}{T}\frac{\partial^2 H}{\partial p \partial T}.\end{aligned}$$

Next, the right hand side.

$$\begin{aligned}\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial p}\right)_T &= \frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial H}{\partial p}\right)_T - \frac{V}{T}\right] \\ &= \frac{1}{T}\frac{\partial^2 H}{\partial T \partial p} + \left(\frac{\partial H}{\partial p}\right)_T\left(\frac{-1}{T^2}\right) - \frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_p + \frac{V}{T^2} \\ &= \frac{1}{T}\left[\frac{\partial^2 H}{\partial T \partial p} - \left(\frac{\partial V}{\partial T}\right)_p\right] - \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial p}\right)_T - V\right].\end{aligned}$$

Equate the left and right hand sides now.

$$\frac{1}{T}\frac{\partial^2 H}{\partial p \partial T} = \frac{1}{T}\frac{\partial^2 H}{\partial T \partial p} - \frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_p - \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial p}\right)_T - V\right].$$

The first two terms will cancel again because of the exactness of the total differential of a state function (in this case H). We are left with

$$\begin{aligned}\frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_p &= -\frac{1}{T^2}\left[\left(\frac{\partial H}{\partial p}\right)_T - V\right] \\ -\left(\frac{\partial V}{\partial T}\right)_p &= \frac{1}{T}\left[\left(\frac{\partial H}{\partial p}\right)_T - V\right].\end{aligned}$$

Replace this into our prior expression for $\left(\frac{\partial S}{\partial p}\right)_T$ to get

$$\boxed{\left(\frac{\partial S}{\partial p}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial p}\right)_T - V\right] = -\left(\frac{\partial V}{\partial T}\right)_p}. \tag{16.11}$$

As last time we can continue simplifying this a little further. Recall that the coefficient of thermal expansion is

$$\begin{aligned} \alpha &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \\ \left(\frac{\partial V}{\partial T}\right)_p &= \alpha V \end{aligned}$$

So that

$$\left(\frac{\partial S}{\partial p}\right)_T = -\alpha V.$$

Putting everything together

$$\boxed{dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp} \tag{16.12}$$

$$\boxed{dS = \frac{C_p}{T} dT - \alpha V\, dp} \tag{16.13}$$

The special case of an ideal gas

The relationships just derived in the previous sections are applicable to any system. They have a particularly simple form when applied to the specific case of an ideal gas. Start with

$$\boxed{dS = \frac{C_V}{T} dT + \frac{\alpha}{\kappa} dV}$$

$$\boxed{dS = \frac{C_p}{T} dT - \alpha V\, dp}$$

where

$$\begin{aligned} \alpha &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \\ \kappa &= -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T. \end{aligned}$$

Since for an ideal gas $pV = nRT$ we can show that (and you did this on a homework a while back)

$$\begin{aligned} \alpha &= \frac{1}{T} \\ \kappa &= \frac{1}{p} \end{aligned}$$

So now the first entropy expression becomes

$$dS = \frac{C_V}{T}dT + \frac{p}{T}dV$$

where this can get rearranged using $p = \frac{nRT}{V}$ to

$$\boxed{dS = \tfrac{C_V}{T}dT + \tfrac{nR}{V}dV}. \tag{16.14}$$

when integrated our final expression is

$$\boxed{\Delta S = C_V \ln \tfrac{T_2}{T_1} + nR \ln \tfrac{V_2}{V_1}.} \tag{16.15}$$

assuming that C_V is constant, which it is for an ideal gas.

The second entropy expression becomes

$$\begin{aligned} dS &= \frac{C_p}{T}dT - \alpha V dp \\ &= \frac{C_p}{T}dT - \frac{V}{T}dp \end{aligned}$$

where this can get rearranged again using $V = \frac{nRT}{p}$

$$\boxed{dS = \tfrac{C_p}{T}dT - \tfrac{nR}{p}dp}. \tag{16.16}$$

Once integrated our final expression is

$$\boxed{\Delta S = C_p \ln \tfrac{T_2}{T_1} - nR \ln \tfrac{p_2}{p_1}} \tag{16.17}$$

where again we assume that C_p is constant, which it is for an ideal gas.

Summary

Ok, so you have seen that S is multifaceted. It has an expression for virtually every occasion. Let's summarize things here in a cliff notes manner.

Variations of entropy with T, constant V

$$dS = \frac{C_V dT}{T}$$

Now using this expression, the entropy at some different (final) temperature T_2 can be related to the entropy at some initial temperature T_1 by

$$\begin{aligned}\Delta S = S_{T_2} - S_{T_1} &= \int_{T_1}^{T_2} \frac{dq_{rev}}{T} \\ &= \int_{T_1}^{T_2} \frac{C_V}{T} dT\end{aligned}$$

giving

$$\Delta S = C_V \ln \frac{T_2}{T_1}.$$

This assumes that C_V is constant.

Variations of entropy with V, constant T

$$dS = \frac{\alpha}{\kappa} dV$$

In the particular case of an ideal gas, we get the following for an isothermal (reversible) expansion: In this case, we know for an ideal gas that $\Delta U = 0$, therefore $q = -w$ and

$$\begin{aligned}w &= -\int p dV \\ &= -\int \frac{nRT}{V} dV \\ &= -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{p_1}{p_2}.\end{aligned}$$

So putting this into our expression for $S = \frac{q_{rev}}{T}$

$$\Delta S = nR \ln \frac{V_2}{V_1} = nR \ln \frac{p_1}{p_2}.$$

Variations of entropy with T, constant p

$$dS = \frac{C_p dT}{T}$$

Now using this expression, the entropy at some different (final) temperature T_2 can be related to the entropy at some initial temperature T_1.

$$\begin{aligned} \Delta S = S_{T_2} - S_{T_1} &= \int_{T_1}^{T_2} \frac{dq_{rev}}{T} \\ &= \int_{T_1}^{T_2} \frac{C_p}{T} dT \end{aligned}$$

giving

$$\Delta S = C_p \ln \frac{T_2}{T_1}$$

if C_p is constant (which it is for an ideal gas). Just like we saw earlier in the Kirchoff's equation section, in reality the heat capacity is not temperature independent. However, as a first approximation you can just assume that it is constant or you can use some mean value over the desired temperature range $\bar{C_p}$. And just like before, if there is a significant variation of C_p with temperature or we want more precision, then we can express C_p through a power series where for example

$$C_p = a + bT + cT^2.$$

Thus

$$\begin{aligned} \Delta S &= \int_{T_1}^{T_2} \frac{C_p}{T} dT \\ &= \int_{T_1}^{T_2} \left(\frac{a}{T} + b + cT \right) dT \end{aligned}$$

giving

$$\Delta S = a \ln \frac{T_2}{T_1} + b\Delta T + \frac{C(T_2^2 - T_1^2)}{2}.$$

Variations of entropy with p, constant T

$$dS = \alpha V dp$$

where in the ideal gas case

$$\alpha = \frac{1}{T}$$

We then get

$$dS = \frac{V}{T}dp = \frac{nR}{p}dp.$$

When integrated you get

$$\Delta S = nR \ln \frac{p_2}{p_1}.$$

Miscellaneous: Variations of entropy with a phase change, constant p

Phase changes provide a straightforward evaluation of the entropy change associated with it since the temperature will be constant and q can be considered reversible. Since we have defined

$$\Delta S = \frac{q_{rev}}{T}$$

for fusion (melting), we get

$$\boxed{\Delta S_{fus} = \frac{\Delta H_{fus}}{T_m}} \tag{16.18}$$

while for vaporization (boiling) we get

$$\boxed{\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}} \tag{16.19}$$

and for sublimation

$$\boxed{\Delta S_{sub} = \frac{\Delta H_{sub}}{T_{sub}}}. \tag{16.20}$$

Trouton's Rule

Ok, I don't really know who Trouton was but he must have been an experimentalist because he made an observation that ΔS_{vap} for many liquids had roughly the same value.

$$\boxed{\Delta S_{vap} \simeq 85 J/molK}. \tag{16.21}$$

After some quick checking I found this reference:
Frederick Thomas Trouton: The Man, the Rule, and the Ratio
The Chemical Educator
Volume 6 Issue 1 (2001) pp 55-61
Looks like there is more to the guy than just this rule. Who knew.

Putting it all together, a thermodynamic cycle

Recall the three step thermodynamic cycle in the first law of thermodynamics chapter. Ok, let's analyze it again and combine all of our knowledge about changes in internal energy, U, enthalpy, H, entropy, S, and work and heat. This is good practice. Practice makes perfect.

The original question was presented as follows. One mole of an ideal (monatomic) gas at an initial temperature of 300K and an initial pressure of 1 atm is taken reversibly through a three step cycle.

Step 1 Isothermal expansion to a volume twice the original volume

Step 2 Constant pressure compression until the original volume is restored

Step 3 Isometric heating until the initial state is reached.

Calculate the work, heat, change in internal energy, enthalpy and entropy for each step of the cycle. What are the net changes of all the above variables for the full cycle?

To do this question correctly, let's tediously construct a PV diagram for each of the three states of the cycle. First we will find the initial volume. I'll call it V_a. **Hint** Anytime you run across 2 of the three state defining variables, (p,T) or (p,V) or (V,T) you can calculate the third variable through the equation of state.

Find V_a first From the equation of state (note the units are liters and atms)

$$(1)(V_a) = (0.08206)(300)$$

thus

$$V_a = 24.6\text{L}.$$

Next, find p_b Since step 1 is isothermal, we know V_b and T_b at the second point of the cycle. We just need the final pressure. Using the equation of state, we get

$$(p_b)(49.236) = (0.08206)(300).$$

Thus

$$p_b = 0.5\text{atm}.$$

Next, find T_c Since we know the volume and pressure at the third state all we need is its temperature. From the equation of state

$$(0.5)(24.62) = (0.08206)(T_c).$$

Thus

$$T_c = 150K$$

Ok, now we're set to go ahead and calculate all of the requested quantities.

Step 1 (isothermal, reversible expansion) The work here is

$$\begin{aligned} w_{a\to b} &= -RT\ln\frac{V_b}{V_a} \\ &= -(8.314)(300)ln(2) \\ &= -1728.85\text{J}. \end{aligned}$$

Next, because we have an ideal gas and an isothermal process (U and H depend only on T for ideal gases)

$$\Delta U_{a\to b} = 0.$$

From the first law of thermodynamics

$$\begin{aligned} q_{a\to b} &= -w \\ &= RT\ln\frac{V_b}{V_a} \\ &= 1728.85\text{J}. \end{aligned}$$

We now need the enthalpy

$$\Delta H_{a\to b} = \Delta U + R\Delta T = 0$$

or

$$\Delta H_{a\to b} = \Delta U + \Delta(pV) = 0.$$

Or you just remember that for an ideal gas that the change in enthalpy is zero if the temperature doesn't change.

I'll illustrate that the top two approaches are equivalent.

Approach 1

$$\begin{aligned} \Delta H_{a\to b} &= \Delta U + R\Delta T \\ &= 0 + (8.314)(0) \\ &= 0. \end{aligned}$$

Approach 2

$$\begin{aligned} \Delta H_{a\to b} &= \Delta U + \Delta(pV) \\ &= \Delta U + p_b V_b - p_a V_a \\ &= 0 + (0.5)(49.236) - (1)(24.62) \\ &= 0 + 24.62 - 24.62 \\ &= 0. \end{aligned}$$

Finally, we want the entropy change

$$\begin{aligned} \Delta S &= \frac{q_{a\to b}}{T_a} = R\ln\frac{V_b}{V_a} \\ &= (8.314)\ln(2) \\ &= 5.763 J/K. \end{aligned}$$

Step 2 (reversible constant pressure compression) The work here is

$$\begin{aligned} w_{b\to c} &= -\int p dV \\ &= -p(V_c - V_b) \\ &= -(0.5)(24.62 - 49.236) \\ &= 12.31 \text{ liter atm} \\ &= 1247.3 J. \end{aligned}$$

Next, we want the heat. This is a constant pressure heating situation so use the constant pressure heat capacity ($C_p = \frac{5}{2}R$ for a monatomic ideal gas).

$$\begin{aligned} q_{b\to c} &= C_p \Delta T \\ &= \frac{5}{2}R(T_c - T_b) \\ &= (2.5)(8.314)(150-300) \\ &= -3117.75 J. \end{aligned}$$

The change of internal energy is thus

$$\begin{aligned} \Delta U_{b\to c} &= q + w \\ &= -1870.65 + 1247.3 \\ &= -1870.45 J. \end{aligned}$$

Next, the enthalpy change is

$$\begin{aligned} \Delta H_{b\to c} &= \Delta U + R\Delta T \\ &= -1870.45 + (8.314)(150-300) \\ &= -1870.45 - 1247.1 \\ &= -3117.55 J. \end{aligned}$$

Finally, we need the entropy change

$$\begin{aligned} dS_{b\to c} &= \frac{q_{b\to c}}{T} \\ &= \frac{C_p dT}{T} \\ \Delta S_{b\to c} &= C_p \ln \frac{T_c}{T_b} \\ &= \frac{5}{2}R \ln \frac{T_c}{T_b} \\ &= (2.5)(8.314)\ln(0.5) \\ &= -14.41 J/K. \end{aligned}$$

Step 3 (isometric heating) Calculate the work first. Since we only deal with PV work and because the volume doesn't change there is no work term

$$w_{c\to a} = 0.$$

Next, calculate the heat. Use the constant volume heat capacity to get

$$\begin{aligned} q_{c\to a} &= C_v(T_2 - T_1) \\ &= \frac{3}{2}R(300-150) \\ &= 1870.65J. \end{aligned}$$

The change in internal energy is then

$$\begin{aligned} \Delta U_{c\to a} &= q + w \\ &= 1870.65 + 0 \\ &= 1870.65J. \end{aligned}$$

The corresponding change in enthalpy is

$$\begin{aligned} \Delta H_{c\to a} &= \Delta U + R\Delta T \\ &= 1870.65 + (8.314)(300-150) \\ &= 1870.65 + 1247.1 \\ &= 3117.75J. \end{aligned}$$

Finally, calculate the change in entropy

$$\begin{aligned} \Delta S_{c\to a} &= \int \frac{C_V dT}{T} \\ &= \frac{3}{2}R\ln\frac{T_a}{T_c} \\ &= (1.5)(8.314)\ln(2) \\ &= 8.644J/K. \end{aligned}$$

Put it all together The net work in the cycle is

$$\begin{aligned} w_{tot} &= w_{a\to b} + w_{b\to c} + w_{c\to a} \\ &= -1728.85 + 1247.3 + 0 \\ &= -481.55J. \end{aligned}$$

The net heat in the cycle is

$$\begin{aligned} q_{tot} &= q_{a\to b} + q_{b\to c} + q_{c\to a} \\ &= 481.75J/mol \end{aligned}$$

Note the small rounding error with this and the work. They are actually the same.

The net internal energy change in the cycle is (you already know what it is but it should still add up to zero. This is a way to check that your calculations have been correct)

$$\begin{aligned}\Delta U_{tot} &= \Delta U_{a\to b} + \Delta U_{b\to c} + \Delta U_{c\to a} \\ &= 0 - 1870.45 + 1870.65 \\ &= 0.\end{aligned}$$

I have some small rounding errors, but it's really zero.

The net change in enthalpy is

$$\begin{aligned}\Delta H_{tot} &= \Delta H_{a\to b} + \Delta H_{b\to c} + \Delta H_{c\to a} \\ &= 0 - 3117.55 + 3117.75 \\ &= 0.\end{aligned}$$

Again, I have some small rounding errors, but it's zero.

Finally, the net change in entropy is

$$\begin{aligned}\Delta S_{tot} &= \Delta S_{a\to b} + \Delta S_{b\to c} + \Delta S_{c\to a} \\ &= 5.763 - 14.41 + 8.64 \\ &= 0.\end{aligned}$$

Done. Fun right?

Stirling cycle

Here is another cycle that I put in here because of the Stirling engine demo that I do each time I teach this class. The idealized Stirling cycle consists of four steps.

- Step 1. Isothermal expansion ($V_1 \rightarrow V_2$) and ($p_1 \rightarrow p_2$)
- Step 2. Isometric (constant volume) cooling (V_2) and ($p_2 \rightarrow p_3$)
- Step 3. Isothermal compression ($V_2 \rightarrow V_1$) and ($p_3 \rightarrow p_4$)
- Step 4. Isometric heating (V_1) and ($p_4 \rightarrow p_1$)

We can calculate the following terms w, q, ΔU, ΔH, and ΔS like before along each step of the cycle. We expect $\Delta U_{net} = 0$, $\Delta H_{net} = 0$, and $\Delta S_{net} = 0$ for the whole cycle since all are state functions. Assume an ideal gas and reversible steps along the isothermal compression and expansion steps.

Step 1

Assume a reversible expansion so that $p_{ext} = p$. Because this is an ideal gas and an isothermal process we immediately say

$$\boxed{\Delta U = 0}$$

$$\boxed{\Delta H = 0}.$$

In addition, we see that $q = -w$. Now, we find the work term

$$\begin{aligned} dw &= -p_{ext} dV \\ &= -p dV \\ &= -\frac{nRT}{V} dV \end{aligned}$$

so that

$$\boxed{w = -nRT_1 \ln \tfrac{V_2}{V_1}.}$$

Likewise

$$\boxed{q = nRT \ln \tfrac{V_2}{V_1}.}$$

Finally,

$$\boxed{\Delta S = \tfrac{q_{rev}}{T} = nR \ln \tfrac{V_2}{V_1}}.$$

Step 2

Since the process is isometric, there can be no pdV work done. As a consequence,

$$\boxed{w = 0}.$$

Also, given that it's a constant volume process $\Delta U = q$ where

$$\boxed{q = -C_V(T_2 - T_1)}.$$

Then

$$\boxed{\Delta U = -C_V(T_2 - T_1)}.$$

The enthalpy term can be found from

$$\boxed{\Delta H = \Delta U + V_2 \Delta p}$$

Ok, here we need an expression for what Δp should look like. We use the ideal gas equations of state

$$\begin{aligned} p_2 V_2 &= nRT_1 \\ p_3 V_2 &= nRT_2 \end{aligned}$$

giving

$$\frac{p_2}{p_3} = \frac{T_1}{T_2}$$

or

$$p_3 = p_2 \left(\frac{T_2}{T_1} \right).$$

The pressure difference, $p_3 - p_2$, is then

$$\Delta p = p_2 \left(\frac{T_2}{T_1} - 1 \right).$$

Finally, $S = f(T, V)$

$$dS = \frac{C_V}{T} dT$$

so that

$$\boxed{\Delta S = C_V \ln \tfrac{T_2}{T_1}}.$$

Step 3

Assume a reversible expansion so that $p_{ext} = p$. Because this is an ideal gas and an isothermal process we immediately say

$$\boxed{\Delta U = 0}$$

$$\boxed{\Delta H = 0}.$$

In addition, we see that $q = -w$. Now, we find the work term

$$\begin{aligned} dw &= -p_{ext}dV \\ &= -pdV \\ &= -\frac{nRT}{V}dV \end{aligned}$$

so that

$$w = -nRT_1 \ln \frac{V_4}{V_2}.$$

Since $V_4 = V_1$ we have

$$\boxed{w = -nRT \ln \tfrac{V_1}{V_2}.}$$

Likewise,

$$q = nRT \ln \frac{V_4}{V_2}$$

and since $V_4 = V_1$ we get

$$\boxed{q = nRT \ln \tfrac{V_1}{V_2}}.$$

Finally,

$$\boxed{\Delta S = \tfrac{q_{rev}}{T} = nR \ln \tfrac{V_1}{V_2}}.$$

Step 4

Since the process is isometric, there can be no pdV work done. As a consequence,

$$\boxed{w = 0}.$$

Also, given that it's a constant volume process $\Delta U = q$ where

$$\boxed{q = -C_V(T_1 - T_2)}.$$

Then

$$\boxed{\Delta U = -C_V(T_1 - T_2)}.$$

The enthalpy term can be found as

$$\boxed{\Delta H = \Delta U + V_4 \Delta p}.$$

Ok, here we need an expression for what Δp should look like. We use the ideal gas equations of state

$$\begin{aligned} p_1 V_1 &= nRT_1 \\ p_4 V_4 &= nRT_2 \end{aligned}$$

but since $V_4 = V_1$ we get the pair

$$\begin{aligned} p_1 V_1 &= nRT_1 \\ p_4 V_1 &= nRT_2 \end{aligned}$$

giving

$$\frac{p_1}{p_4} = \frac{T_1}{T_2}.$$

The pressure difference, $p_1 - p_4$, is then

$$\Delta p = p_4 \left(\frac{T_1}{T_2} - 1 \right).$$

Finally, we can relate p_4 to p_2 through p_3 since we will need this shortly

$$p_4 V_4 = p_3 V_3$$

but since $V_3 = V_2$ we get

$$p_4 V_4 = p_3 V_2.$$

Next, since $V_4 = V_1$ we get

$$p_4 V_1 = p_3 V_2$$

or that $p_4 = \frac{V_2}{V_1} p_3$. Finally, recall that in step 2 we found $p_3 = \frac{T_2}{T_1} p_2$.

The entropy change is

$$dS = \frac{C_V}{T} dT$$

giving

$$\boxed{\Delta S = C_V \ln \tfrac{T_1}{T_2}}.$$

Summary

Let's put it all together now to prove explicitly that $\Delta U_{net} = 0$, $\Delta H_{net} = 0$, and $\Delta S_{net} = 0$

For ΔU_{net}

$$\begin{aligned}
\Delta U_{12} &= 0 \\
\Delta U_{23} &= -C_V(T_2 - T_1) \\
\Delta U_{34} &= 0 \\
\Delta U_{41} &= -C_V(T_1 - T_2) = C_V(T_2 - T_1)
\end{aligned}$$

Therefore

$$\Delta U_{net} = 0.$$

For ΔH_{net}

$$\begin{aligned}
\Delta H_{12} &= 0 \\
\Delta H_{23} &= -C_V(T_2 - T_1) + V_2 p_2 \left(\frac{T_2}{T_1} - 1\right) \\
\Delta H_{34} &= 0 \\
\Delta H_{41} &= -C_V(T_1 - T_2) + V_4 p_4 \left(\frac{T_1}{T_2} - 1\right)
\end{aligned}$$

You can see that the last term is the negative of the second term by recalling that $V_4 = V_1$, $p_4 = \frac{V_2}{V_1} p_3$ and $p_3 = \frac{T_2}{T_1} p_2$. When put together you get

$$\Delta H_{41} = C_V(T_2 - T_1) - V_2 p_2 \left(\frac{T_2}{T_1} - 1\right)$$

so that when everything is added up

$$\Delta H_{net} = 0.$$

For ΔS_{net}

$$\begin{aligned}\Delta S_{12} &= nR\ln\frac{V_2}{V_1}.\\ \Delta S_{23} &= C_V\ln\frac{T_2}{T_1}.\\ \Delta S_{34} &= nR\ln\frac{V_1}{V_2}.\\ \Delta S_{41} &= C_V\ln\frac{T_1}{T_2}.\end{aligned}$$

When everything is added up, we see that

$$\Delta S_{net} = 0.$$

The Carnot cycle

Here is another cycle commonly seen since in engineering thermodynamics we talk about efficiencies. Let's run this cycle for fun and focus on the entropy changes. The Carnot cycle was conceived by a French engineer called Sadi Carnot and consists of 4 reversible stages. It is usually evaluated using an ideal gas. The four steps of the cycle are

- **Step 1**: Reversible isothermal expansion of a gas from state A to state B.
- **Step 2**: Reversible adiabatic expansion of a gas from state B to state C.
- **Step 3**: Reversible isothermal compression of a gas from state C to state D.
- **Step 4**: Reversible adiabatic compression of a gas from state D to state A.

Step 1 Since we're dealing with an ideal gas and the process is isothermal $\Delta U = 0$ and $\Delta H = 0$. Then $q + w = 0$ or $q = -w$. Next $w = -\int pdV$ since this is a reversible process. Then because the gas is ideal $p = \frac{nRT}{V}$. The work and heat done by the gas expanding is therefore

$$\begin{aligned} w &= -nRT\ln\frac{V_b}{V_a}\\ q &= nRT\ln\frac{V_b}{V_a}.\end{aligned}$$

The associated entropy change is

$$
dS = \frac{dq_{rev}}{T}
$$
$$
\Delta S = \frac{q_{rev}}{T}
$$

where dq_{rev} is found from above. The corresponding entropy change is

$$
\Delta S_{A \to B} = nR \ln \frac{V_b}{V_a}.
$$

Step 2 This is an adiabatic expansion. Therefore $q = 0$ and $w = -\int pdV$ (reversible), $\Delta U = w$ (first law), and $\Delta H = \Delta U + nR\Delta T$. The work is

$$
\begin{aligned}
w &= -\int pdV \\
&= \int C_V dT \\
&= C_V(T_2 - T_1).
\end{aligned}
$$

Now, the corresponding entropy change is

$$
\Delta S_{B \to C} = 0
$$

since this was an adiabatic reversible process. You can see this from $dS = \frac{dq_{rev}}{T}$. Irrespective of what T is the numerator will always be zero.

Step 3 This is an isothermal process so $\Delta U = 0$, $\Delta H = 0$ and $q = -w$ where

$$
\begin{aligned}
w &= -\int_{V_c}^{V_d} pdV \\
&= -nRT \int_{V_c}^{V_d} \frac{dV}{V} \\
&= -nRT \ln \frac{V_d}{V_c}.
\end{aligned}
$$

Note that in this case that $V_d < V_c$. The corresponding heat is

$$
q = nRT \ln \frac{V_d}{V_c}.
$$

The entropy change is then

$$
\Delta S = \frac{q_{rev}}{T}
$$

giving

$$\Delta S_{C\rightarrow D} = nR\ln\frac{V_d}{V_c}.$$

Step 4 Another adiabatic step. Immediately $q = 0$, $\Delta U = w$, and $\Delta H = \Delta U + nR\Delta T$. The work in this step is

$$\begin{aligned} w &= -\int pdV \\ &= \int C_V dT \\ &= C_V(T_1 - T_2). \end{aligned}$$

The associated entropy change is

$$\Delta S_{D\rightarrow A} = 0$$

since this was an adiabatic reversible step. You can see this from $dS = \frac{dq_{rev}}{T}$. Irrespective of what T is the numerator will always be zero.

Putting it all together The total entropy change of the cycle is

$$\begin{aligned} \Delta S_{tot} &= nR\ln\frac{V_b}{V_a} + 0 + nR\ln\frac{V_d}{V_c} + 0 \\ &= nR\left(\ln\frac{V_b}{V_a} + \ln\frac{V_d}{V_c}\right) \\ &= nR\ln\left(\frac{V_bV_d}{V_aV_c}\right). \end{aligned}$$

Did we make a mistake? Why isn't this zero? Not to worry, recall from our earlier work on adiabatic processes

$$V_{final}T_{final} = V_{initial}T_{initial}$$

So in step 2

$$\begin{aligned} V_cT_2 &= V_bT_1 \\ \frac{T_2}{T_1} &= \frac{V_b}{V_c}. \end{aligned}$$

Likewise, in step 4

$$\begin{aligned} V_aT_1 &= V_dT_2 \\ \frac{T_2}{T_1} &= \frac{V_a}{V_d}. \end{aligned}$$

Therefore

$$\frac{V_a}{V_d} = \frac{V_b}{V_c}$$

or

$$\frac{V_b V_d}{V_a V_c} = 1.$$

Therefore, with regards to the total entropy

$$\begin{aligned} \Delta S_{tot} &= nR\ln\left(\frac{V_b V_d}{V_a V_c}\right) \\ &= nR\ln(1) \\ &= 0. \end{aligned}$$

Done. In the Carnot, or another cycle, the total entropy change is zero. This demonstrates that S is a state function. I suppose you could also prove that U and H are also state functions using the Carnot cycle. As an example, the total internal energy change around the cycle should be zero. You can simply add up all the ΔU terms for each step or you can sum the total work and total heat. Let's see this alternate procedure since it should yield the same thing as summing all the internal energy changes. The total work in the cycle is

$$\begin{aligned} w_{tot} &= w_1 + w_2 + w_3 + w_4 \\ &= -nRT_1 \ln\frac{V_b}{V_a} + C_V(T_2 - T_1) - nRT_2 \ln\frac{V_d}{V_c} - C_V(T_2 - T_1) \\ &= -nRT_1 \ln\frac{V_b}{V_a} - nRT_2 \ln\frac{V_d}{V_c}. \end{aligned}$$

The total heat in the cycle is

$$\begin{aligned} q_{tot} &= q_1 + q_2 + q_3 + q_4 \\ &= nRT_1 \ln\frac{V_b}{V_a} + 0 + nRT_2 \ln\frac{V_d}{V_c} + 0 \\ &= nRT_1 \ln\frac{V_b}{V_a} + nRT_2 \ln\frac{V_d}{V_c}. \end{aligned}$$

You can see that the sum of work and heat will be zero. The internal energy is therefore a state function. I'll let you do ΔH_{net} on your own.

The efficiency of the cycle

Finally, not that we're engineers but one can write down the efficiency of a Carnot cycle or heat engine as follows. The efficiency of a heat engine ϵ is defined as the ratio of work done on the surroundings to the heat input at the higher temperature.

$$\begin{aligned}\epsilon &= \frac{-w_{tot}}{q_1}\\ &= \frac{q_1+q_3}{q_1}\\ &= 1+\frac{q_3}{q_1}\end{aligned}$$

where $q_3 = nRT_2 \ln \frac{V_d}{V_c}$ and $q_1 = nRT_1 \ln \frac{C_b}{V_a}$. Therefore,

$$\epsilon = 1 + \frac{T_2 \ln \frac{V_d}{V_c}}{T_1 \ln \frac{V_b}{V_a}}.$$

Using our previous adiabatically derived relationships between volumes

$$\frac{V_a}{V_d} = \frac{V_b}{V_c}$$

we rearrange to get

$$\frac{V_d}{V_c} = \frac{V_a}{V_b}.$$

As a consequence, you can see that the ratio of natural logarithms in ϵ will disappear and we will be left with our desired final expression for the efficiency

$$\begin{aligned}\epsilon &= 1+\frac{T_2}{T_1}\frac{\ln \frac{V_d}{V_c}}{\ln \frac{V_b}{V_a}}\\ &= 1+\frac{T_2}{T_1}\frac{\ln \frac{V_d}{V_c}}{\ln \frac{V_c}{V_d}}\\ &= 1-\frac{T_2}{T_1}\frac{\ln \frac{V_d}{V_c}}{\ln \frac{V_d}{V_c}}.\end{aligned}$$

This gives

$$\epsilon = 1 - \frac{T_2}{T_1}$$

and you can see that the efficiency is not 1.

The third law of thermodynamics

This is stated a number of ways but all with same intent. "*As the temperature approaches absolute zero so does the entropy of a system*" or "*The entropy of a perfect crystal at zero Kelvin is zero*" or "*One cannot achieve absolute 0K*". **Bottom line at 0K there is no disorder and hence the entropy of anything is zero there.** This is important because for the first time we see one of these important state functions actually have an absolute value. Recall that U and H were always considered within the context of changes, not absolute values.

Qualitative rules for entropy changes in reactions

Even without knowing values for the entropies of substances you can sometimes predict the sign of ΔS for a reaction. The entropy will usually increase in the following situations.

- A reaction in which a molecule is broken into two or more smaller species
- A reaction in which there is an increase in the number of moles of gas
- A process in which a solid changes to a liquid or gas; a liquid changes to a gas.

Entropy changes in chemical reactions

We come back to something that is akin to thermochemistry except with entropies. First, entropy is a state function. As a consequence, you can take a Hess type approach (don't recommend) to find the entropy change for some chemical reaction of interest. This means we need the entropy changes for a bunch of sub reactions, which we will sequentially add up to get the total entropy change of the main reaction. Alternatively, you can look up the entropy changes of the products and reactants, get the stoichiometry right, then take the difference, final minus initial. Simple. All we need are so-called standard entropies, which are similar in spirit to the heats of formation of different substances.

So, in practice, you just look up the standard entropies S^o_{298} of a desired compound in a table. These are molar entropies at 298K and 1 bar pressure. The nice thing here is that these are actually absolute, not relative, values because the Third Law of Thermodynamics provides an absolute reference floor for the entropy of any substance.

If you are hardcore, you could go and calculate these standard entropies yourself. Let's illustrate this once and only once. (but ultimately why bother, especially since you can look them up. Nonetheless it's informative to see the guts of what has to be done.)

Example

Consider a gas at room temperature. In order to obtain its standard entropy S^o_{298} we need to determine the entropy change in taking 1 mol of this gas through the following steps at constant pressure (1 bar).

Step 1 Heat the gas from 0K to the melting point of the solid T_m

$$\Delta S^o_1 = \int_0^{T_m} \frac{C_p(s)dT}{T}.$$

Note that some extrapolation to 0K is needed here if $C_p(s)$ is a constant. Recall that this in itself is an approximation.

Step 2 Next, undergo a phase transition at the melting point

$$\Delta S^o_2 = \frac{\Delta H_{fus}}{T_m}.$$

Step 3 Heat the liquid from T_m to its boiling point T_b (constant p).

$$\Delta S^o_3 = \int_{T_m}^{T_b} \frac{C_p(liq)dT}{T}.$$

Step 4 Then undergo a phase transition at the boiling point

$$\Delta S^o_4 = \frac{\Delta H_{vap}}{T_b}.$$

Step 5 Heat the gas from the boiling temperature to 298K (constant p)

$$\Delta S^o_5 = \int_{T_b}^{298} \frac{C_p(g)dT}{T}.$$

Step 6 Finally add everything together to get the desired standard entropy.

$$\Delta S^o_{298} = \Delta S^o_1 + \Delta S^o_2 + \Delta S^o_3 + \Delta S^o_4 + \Delta S^o_5.$$

Entropy changes in reactions

This is exactly the same procedure as done with enthalpy in the Thermochemistry section (remember, the easy way). You add up the enthalpy changes of the product, add up the enthalpy changes of the reactants, take stoichiometry into account, then take the difference, final minus initial.

For those math aficionados the formal definition is

$$\Delta S^o_{298}(\text{rxn}) = \sum \nu_i S^o_{298}(\text{prod}) - \sum \nu_i S^o_{298}(\text{react})$$

so for the particular case

$$\alpha A + \beta B \rightarrow \gamma C + \delta D$$

we have

$$\Delta S^o_{298} = [\gamma S^o_{298}(C) + \delta S^o_{298}(D)] - [\alpha S^o_{298}(A) + \beta S^o_{298}(B)].$$

Finally needless to say, there will be times when you will need the entropy change at a different temperature -not 25^oC. When you need to do this, just take a Kirchoff's equation approach to calculate the additional change in entropy incurred by changing the temperature. You can calculate each individual temperature induced entropy change or you can (like in the Thermochemistry section) lump all the C_p values together, take into account the stoichiometry, and then use the net C_p to calculate the temperature induced entropy change for the entire reaction. I recommend this latter approach. It is much faster.

Example

Using data from some table, calculate the entropy change at 25^{o}C and at 750^{o}C for the following reaction at 1 bar.

$$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g).$$

Ans:

$$\begin{aligned} C(\text{graphite}) + O_2(g) &\rightarrow CO_2(g) \\ 5.7 + 205.1 &\rightarrow 213.7 \end{aligned}$$

$$\begin{aligned} \Delta S_{298} &= 213.7 - (5.7 + 205.1) \\ &= 2.9 J/K. \end{aligned}$$

Now at 750^oC (1023.15 K)

$$\Delta S_{750} = \Delta S_{25} + C_p(net) \ln \frac{T_2}{T_1}.$$

Since we are dealing with a ratio, you don't have to work in Kelvin. You could do this in C if you wanted to.

$$\Delta S_{750} = 2.9 + C_p(net) \ln \frac{1023.15}{298.15}$$

where now the net heat capacity is

$$\begin{aligned} C_p &= [C_p(CO_2) - C_p(\text{graphite}) - C_p(O_2)] \\ &= 37.1 - 8.5 - 29.4 \\ &= -0.8 J/K. \end{aligned}$$

Thus,

$$\begin{aligned} \Delta S_{750} &= 2.9 - 0.8 \ln(3.43) \\ &= 1.916 J/K. \end{aligned}$$

Entropy and the environment

This last section shows that sometimes something determined via system entropy alone might seem counterintuitive, especially if trying to predict the spontaneity of a process for a non-isolated system. In this case, one must consider the change of the surrounding's entropy as well. (Or to foreshadow, this example will show the need for something better than just entropy to predict spontaneity. This will lead us into the development of what are called Gibbs and Helmholtz Free Energies.)

Consider the entropy change for a familiar chemical reaction.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l).$$

The change in entropy as determined from a table is (all units J/mol K)

$$\begin{aligned} 2H_2(g) + O_2(g) &\rightarrow 2H_2O(l) \\ 2(130.7) + 205.1 &\rightarrow 2(69.9) \end{aligned}$$

is

$$\Delta S^o_{298} = -326.7 J/K.$$

Ok, so what's wrong here? Well, you can see that there is a loss of entropy on forming water as would be expected in a reaction involving 3 moles of disordered high entropy gas forming 2 mols of a lower entropy liquid. How can this be? We know that water is stable at 298K and this reaction occurs spontaneously. Doesn't this contradict the Second Law of Thermodynamics?

Well, the second law in its various forms says that the entropy of the universe (system + surroundings) will increase for a spontaneous process in the cae of a non-isolated system. As a consequence, we need to know the entropy change of the surroundings.

The enthalpy change in making 2 moles of water is $\Delta H_f^o = -285.8kJ$. The corresponding enthalpy change of the surroundings is the negative of this value $\Delta H_{surr} = 285.8kJ$ given that p is constant and $-q_{rev} = \Delta H_{surr}$. **We will assume that interactions with the surroundings always occur in a reversible manner**, allowing us to use

$$\Delta S_{surr} = \frac{q_{rev}}{T}$$

where

$$\begin{aligned} \Delta S_{surr} &= \frac{\Delta H_{surr}}{T} \\ &= \frac{2(285.8kJ)}{298.15K} \\ &= 1.92kJ/K. \end{aligned}$$

The total entropy change is then

$$\begin{aligned} \Delta S_{tot} &= \Delta S_{sys} + \Delta S_{surr} \\ &= 1593.3J/K. \end{aligned}$$

So you see that there is an overall increase in the total entropy of the universe in agreement with the second law. Obviously, there must be a better way to do this. Thus, we will introduce the Gibbs and Helmholtz free energies in the next chapter.

Chapter 17

Free energy (Helmholtz and Gibbs)

There's no such thing as free lunch, or is there?

Processes at constant T and p, the Gibbs free energy

We saw in the previous section dealing with entropy that for a spontaneous process at constant T and p

$$\begin{aligned}\Delta S_{universe} &= \Delta S_{sys} + \Delta S_{surr} \geq 0 \\ &= \Delta S_{sys} - \frac{\Delta H_{sys}}{T} \geq 0 \\ & T\Delta S_{sys} - \Delta H_{sys} \geq 0.\end{aligned}$$

Rearrange this expression a little bit

$$-T\Delta S_{sys} + \Delta H_{sys} \leq 0$$

to get

$$\Delta H_{sys} - T\Delta S_{sys} \leq 0.$$

At this point, we can introduce a new function

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} \leq 0$$

and call it the Gibbs free energy. Namely,

$$\boxed{G = H - TS} \tag{17.1}$$

where at constant temperature, T, and pressure, p

$$\boxed{\Delta G = \Delta H - T\Delta S}. \tag{17.2}$$

Note that unlike the end of the last section where we had to consider the changes occurring in both the systems and its surroundings, the Gibbs free energy takes care of this. Everything is now expressed in terms of the system's free energy change. Hence this will be a new more *convenient* criteria for determining the spontaneity of a process.

We can make the following statement then "*A spontaneous process is one where at constant T and p, the Gibbs free energy decreases* $\Delta G < 0$". Note that G has units of energy, kJ/mol. Also, just like all the other thermodynamic quantities we have been talking about, what we really care about are free energy differences, not absolute values.

Processes at constant T and V, Helmholtz free energy

Note that the above argument has been developed under constant temperature and pressure conditions. An analogous argument can be made for the case of constant temperature and volume conditions.

We saw in the previous section dealing with entropy that for a spontaneous process

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr} \geq 0$$

This time, however, we are not at constant temperature and pressure but rather at constant temperature and volume. The only difference then is that $\Delta S_{surr} = -\frac{\Delta U_{sys}}{T}$ since at constant volume $dq = dU$. We get

$$\begin{aligned} \Delta S_{universe} &= \Delta S_{sys} - \frac{\Delta U_{sys}}{T} \geq 0 \\ &= T\Delta S_{sys} - \Delta U_{sys} \geq 0. \end{aligned}$$

At this point, rearrange this expression a little bit to get

$$\Delta U_{sys} - T\Delta S_{sys} \leq 0.$$

Since the temperature is constant, we can add the term $-S\Delta T$ to both sides of the expression (In the prior ΔG expression you could have also done this trick.)

$$\begin{aligned}\Delta U_{sys} - T\Delta S_{sys} - S\Delta T &\leq 0 \\ \Delta U - \Delta(TS) &\leq 0 \\ \Delta(U - TS) &\leq 0\end{aligned}$$

and we now introduce a new state function called the Helmholtz free energy, A.

$$\boxed{A = U - TS} \tag{17.3}$$

where at constant T and V

$$\boxed{\Delta A = \Delta U - T\Delta S}. \tag{17.4}$$

Again, like the Gibbs free energy you have implicitly taken care of changes in the surroundings when looking at ΔA. Everything is now expressed in terms of the system. Hence this and the Gibbs free energy are much more convenient ways to predict spontaneity.

We can make the following statement "*A spontaneous process is one where at constant T and V, the Helmholtz free energy decreases* $\Delta A < 0$".

Now since most chemical reactions occur at constant pressure, frankly, we use ΔG way more often. ΔA however, can be useful especially when dealing with solids or condensed phase processes where ΔV is negligibly small. Are you starting to see the parallels?

Note that now in terms of predicting spontaneity for some process using ΔG and ΔA, you have to consider ΔH, ΔS and T. They will all dictate whether something is spontaneous or not (i.e. $\Delta G < 0$ or $\Delta A < 0$).

For example, at low temperatures T, the $T\Delta S$ term in the Gibbs free energy may be small compared to ΔH. If so, then ΔG is insensitive to ΔS. Conversely, at high temperatures, the $T\Delta S$ term might be pretty big, so large that it overwhelms any ΔH term. So at high temperatures, the ΔS term might now control whether a process is spontaneous or not. An analogous argument applies to ΔA as you can guess. This is probably why you have gotten the impression that exothermic processes are spontaneous since, in some cases, ΔH overwhelms $T\Delta S$ in our expression for ΔG.

Relationship between G and A

From the definition of G we have

$$\begin{aligned} G &= H - TS \\ &= (U + pV) - TS \\ &= (U - TS) + pV \\ &= A + pV. \end{aligned}$$

Thus, the relationship between G and A is

$$\boxed{G = A + pV}. \tag{17.5}$$

Variations in Gibbs free energy, preliminaries

For a one component system (i.e. one pure substance. The reason for this distinction is that in the future we will begin to talk about mixtures), let's see how temperature and pressure might affect the Gibbs free energy. This derivation will be repeated in the next section and a mnemonic will be provided to help you remember the expression. We begin with

$$\begin{aligned} G &= H - TS \\ G &= (U + pV) - TS \\ dG &= dU + pdV + Vdp - TdS - SdT \end{aligned}$$

where from the first law of thermodynamics $dU = dq + dw$. Next, if only reversible pV work is done $dw = -pdV$. The reason I can arbitrarily invoke a reversible path is that since G is a state function, I can construct whatever path I want from the initial to the final state. The ΔG expression I come up with will be the same for any other possible path between the same initial and final states. Now, from the thermodynamic definition of entropy we have $dS = \frac{dq}{T}$ or $dq = TdS$. Thus

$$dU = TdS - pdV$$

(By the way, this total differential is one of the fundamental equations of thermodynamics. We will come back to this in the next section). Replace this dU expression back into our expression for dG to get

$$\boxed{dG = Vdp - SdT}. \tag{17.6}$$

Through this expression (another total differential), you can see the change of free energy with temperature and pressure.

Variation in Gibbs free energy with temperature, constant pressure, $G(T,p)$

We will show several expression one can use

First one At constant pressure $dp = 0$ and the previous fundamental equation reduces to

$$dG = -SdT$$

or that

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_p = -S}. \tag{17.7}$$

So you can see that if we know the entropy changes of a substance, we can find out how G varies with temperature. An alternate interpretation is that a measurement of the temperature dependence of G will allow us to calculate S.

By the same token, an analogous expression, particularly useful when dealing with chemical reactions, is

$$\boxed{\left(\frac{\partial \Delta G_{rxn}}{\partial T}\right)_p = -\Delta S_{rxn}}. \tag{17.8}$$

Here ΔG is the change in Gibbs free energy (products minus reactants) and so too is ΔS. You can rationalize this as follows. Consider some generic reaction

$$A + B \rightleftharpoons C + D.$$

For each reactant or product, we have $\left(\frac{\partial G}{\partial T}\right)_p = -S$. Namely,

$$\begin{aligned} \left(\frac{\partial G_A}{\partial T}\right)_p &= -S_A \\ \left(\frac{\partial G_B}{\partial T}\right)_p &= -S_B \\ \left(\frac{\partial G_C}{\partial T}\right)_p &= -S_C \\ \left(\frac{\partial G_D}{\partial T}\right)_p &= -S_D. \end{aligned}$$

So if we sum the product contributions and subtract the sum of the reactant contributions we get

$$\left(\frac{\partial G_C}{\partial T}\right)_p + \left(\frac{\partial G_D}{\partial T}\right)_p - \left[\left(\frac{\partial G_A}{\partial T}\right)_p + \left(\frac{\partial G_B}{\partial T}\right)_p\right] = S_C + S_D - [S_A + S_B]$$

or

$$\left(\frac{\partial \Delta G_{rxn}}{\partial T}\right)_p = -\Delta S_{rxn}.$$

Second one Starting with the above expression, we can rearrange things to get what is known as the Gibbs-Helmholtz equation. Since $G = H - TS$

$$\begin{aligned}
\left(\frac{\partial G}{\partial T}\right)_p &= -S \\
\left(\frac{\partial G}{\partial T}\right)_p &= \frac{G-H}{T} \\
\left(\frac{\partial G}{\partial T}\right)_p &= \frac{G}{T} - \frac{H}{T} \\
\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} &= -\frac{H}{T}.
\end{aligned}$$

Now, the term on the left hand side of the expression is actually $T\left[\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right]_p$. We can show this explicitly.

“Proof”:

$$\begin{aligned}
\left[\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right]_p &= \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p + G\frac{d(1/T)}{dT} \\
&= \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} \\
&= \frac{1}{T}\left[\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T}\right].
\end{aligned}$$

So back to our original expression, we have

$$T\left[\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right]_p = -\frac{H}{T}$$

or that

$$\boxed{\left[\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right]_p = -\frac{H}{T^2}.} \tag{17.9}$$

This equation is referred to as the Gibbs-Helmholtz equation. I guess you can remember it by the name because Gibbs is for the G and use the H in Helmholtz to refer to the enthalpy. It's a relation between G and H.

Since we will likely use the Gibbs-Helmholtz equation frequently, I want to introduce a slight notational change. If instead of using G and H above, we replace them with ΔG and ΔH, an alternative expression is

$$\boxed{\left[\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right]_p = -\frac{\Delta H}{T^2}}. \tag{17.10}$$

The reason for this change is simply that we really don't have absolute values of G or H. In all cases, we're really just speaking about are differences of G and H, in this case relative to so-called standard states. We already saw what this was for enthalpy. We will see this shortly for the free energy. Thus, G above is really ΔG. Ditto for ΔH.

You can see the potential usefulness of the expression since this equation can get integrated to calculate ΔG at another temperature assuming that ΔH is independent of temperature. Namely,

$$\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} = \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

and we find that

$$\boxed{\frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}. \tag{17.11}$$

Now, for reactions, say $aA + bB \rightarrow cC + dD$ where we will encounter equilibria, it will be seen later on that $\Delta G = -RT\ln K_{eq}$ where K_{eq} is the equilibrium constant (actually it is K_p, the equilibrium constant using pressures). One can then substitute this expression for ΔG into the Gibbs-Helmholtz equation to find

$$\boxed{\left(\frac{\partial(\ln K_{eq})}{\partial T}\right)_p = \frac{\Delta H}{RT^2}}. \tag{17.12}$$

When integrated we get

$$\ln K_{eq}(T_2) - \ln K_{eq}(T_1) = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

or more compactly as

$$\boxed{\ln\frac{K_{eq}(T_2)}{K_{eq}(T_1)} = -\frac{\Delta H}{R}\left(\frac{1}{T_2}-\frac{1}{T_1})\right)}. \tag{17.13}$$

The above equation has a name and is called the Vant Hoff equation. But you can see that it is basically the Gibbs-Helmholtz equation.

Note that some authors write the Gibbs-Helmholtz equation differently. Since $d\frac{1}{T} = -\frac{1}{T^2}dT$ you can replace ∂T with $-T^2\partial(1/T)$ to get another version of the Gibbs-Helmholtz equation

$$\boxed{\left(\frac{\partial(\frac{G}{T})}{\partial(\frac{1}{T})}\right)_p = H}. \tag{17.14}$$

When you integrate this expression, you get the same thing we just saw above. Namely,

$$\frac{G(T_2)}{T_2} - \frac{G(T_1)}{T_1} = H\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

or

$$\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} = \Delta H\left(\frac{1}{T_2}-\frac{1}{T_1}\right).$$

Again, all I have done for this last expression is to acknowledge that we don't deal with absolute values of G and H. So G above is really ΔG and ditto for ΔH.

Third one Finally, you can go back to the definition of G, $G = H - TS$. Let's consider the first temperature and call it T_1. Then we get

$$G(T_1) = H - T_1 S$$

or

$$\Delta G(T_1) = \Delta H - T_1\Delta S.$$

Now, if we change temperature to T_2 we have

$$\Delta G(T_2) = \Delta H(T_1 \to T_2) - T_2\Delta S(T_1 \to T_2).$$

So here all we need to know it the temperature dependences of the enthalpy and the entropy. But we know these. Recall that under constant pressure conditions

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$
$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}.$$

Thus

$$\begin{aligned}\Delta G(T_2) &= \Delta H(T_1 \rightarrow T_2) - T_2 \Delta S(T_1 \rightarrow T_2) \\ &= \left[\Delta H(T_1) + \int_{T_1}^{T_2} C_p dT\right] - T_2 \left[\Delta S(T_1) + \int_{T_1}^{T_2} \frac{C_p}{T} dT\right]\end{aligned}$$

The desired expression is then

$$\boxed{\Delta G(T_2) = \left[\Delta H(T_1) + \textstyle\int_{T_1}^{T_2} C_p dT\right] - T_2 \left[\Delta S(T_1) + \textstyle\int_{T_1}^{T_2} \frac{C_p}{T} dT\right]} \quad (17.15)$$

Thus, there are various ways to calculate the Gibbs free energy dependence on temperature, depending on whether ΔH or ΔS of C_p is known.

Variation in Gibbs free energy with pressure, constant temperature, $G(T, p)$

Starting from the fundamental equation for the Gibbs free energy ($dG = V dp - S dT$), when $dT = 0$ we get

$$dG = V dp$$

or that

$$\boxed{\left(\tfrac{\partial G}{\partial p}\right)_T = V}. \quad (17.16)$$

As noted previously the molar volumes of solids and liquids change very little during reactions so for the case of condensed phases we can generally integrate this to get

$$\Delta G = V \Delta p.$$

For a chemical reaction, say

$$A + B \rightleftharpoons C + D$$

we can get an identical expression

$$\boxed{\left(\frac{\partial \Delta G_{rxn}}{\partial p}\right)_T = \Delta V_{rxn}}. \tag{17.17}$$

This can be seen since for each reactant or product we have $\left(\frac{\partial G}{\partial p}\right)_T = V$ giving

$$\begin{aligned}
\left(\frac{\partial G_A}{\partial p}\right)_T &= V_A \\
\left(\frac{\partial G_B}{\partial p}\right)_T &= V_B \\
\left(\frac{\partial G_C}{\partial p}\right)_T &= V_C \\
\left(\frac{\partial G_D}{\partial p}\right)_T &= V_D.
\end{aligned}$$

Summing up the product contributions and subtracting the reactant contributions then gives

$$\left(\frac{\partial G_C}{\partial p}\right)_T + \left(\frac{\partial G_D}{\partial p}\right)_T - \left[\left(\frac{\partial G_A}{\partial p}\right)_T + \left(\frac{\partial G_B}{\partial p}\right)_T\right] = V_C + V_D - [V_A + V_B].$$

This reduces to

$$\left(\frac{\partial \Delta G_{rxn}}{\partial p}\right) = \Delta V_{rxn}.$$

Special case of an ideal gas

Gases are, however, different. Their volume is very sensitive to the external pressure. Consider the case of an ideal gas

$$\begin{aligned}\left(\frac{\partial G}{\partial p}\right)_T &= V \\ &= \frac{nRT}{p} \\ dG &= \frac{nRT}{p}dp \\ \Delta G &= \int \frac{nRT}{p}dp \\ &= nRT\int\frac{dp}{p} \\ &= nRT\ln\frac{p_2}{p_1}.\end{aligned}$$

The desired final expression for the dependence of G with pressure under constant temperature conditions is

$$\boxed{\Delta G = nRT\ln\frac{p_2}{p_1}}. \tag{17.18}$$

Alternatively, you can write this as

$$\begin{aligned}G_2 - G_1 &= nRT\ln\frac{p_2}{p_1} \\ G_2 &= G_1 + nRT\ln\frac{p_2}{p_1}.\end{aligned}$$

Now, if G_1 happens to be the standard free energy (actually the free energy difference relative to a standard state) at 1 bar and 25^oC (G_f^o) this becomes

$$G = G_f^o + nRT\ln\frac{p_2}{1bar}$$

or more simply

$$\boxed{G = G_f^o + nRT\ln\frac{p}{p^o}} \tag{17.19}$$

We will see a similar expression later when dealing with mixtures and what is called the chemical potential. This is why I introduce the notation here. Note that p is the pressure of the gas alone and p^o means 1 bar. Furthermore, I want to reiterate that we're not dealing with absolute values of G. They are actually referenced to a so-called standard state. Hence, more formally, we should replace G (G_f^o) above with ΔG (ΔG_f^o) giving

$$\boxed{\Delta G = \Delta G_f^o + nRT \ln \tfrac{p}{p^o}}. \tag{17.20}$$

Fugacity, real gases

At some point, we will want to consider real systems, not necessarily ideal ones. But what we want to do here is preserve as much of the notation and formulas just derived.

First, a slight notational change that will become important later, not here. On many occasions the term chemical potential is used. The symbol for chemical potential is μ. In the case of pure compounds, the chemical potential is the **same** as the **molar** Gibbs free energy.

$$\boxed{\mu = \tfrac{G}{n}} \tag{17.21}$$

or

$$\mu_{pure} = G.$$

It's just a notational change. However, the chemical potential will become important when dealing with mixtures of compounds. We will see this later. Finally, as you have seen earlier, we're not dealing with absolute values of G or μ here. Understood is that they are actually differences in free energy relative to a standard state. **But, by convention, from here on out you will only see written G or μ in our equations.**

Now, in the case of a real gas where we want an expression for the chemical potential μ, we have just seen that for the ideal gas case (constant temperature so the $-SdT$ term is gone)

$$\boxed{\mu = \mu^o + RT \ln \tfrac{p}{p^o}}. \tag{17.22}$$

Here, we have just flipped over from $G \rightarrow \mu$. It turns out that the real gas case looks very similar

$$\boxed{\mu = \mu^o + RT \ln \tfrac{f}{p^o}} \tag{17.23}$$

where f is an effective pressure called the fugacity

$$\boxed{f = \phi p}. \tag{17.24}$$

In the expression, ϕ is a fudge factor called the fugacity coefficient (it's a measure of nonideality, also some authors use the letter γ). Let's plug this in and see what we get

$$\begin{aligned} \mu &= \mu^o + RT\ln\frac{\phi p}{p^o} \\ &= \left[\mu^o + RT\ln\frac{p}{p^o}\right] + RT\ln\phi \end{aligned}$$

So the final expression for a real gas Gibbs free energy or chemical potential is just the ideal value plus $RT\ln\phi$

$$\boxed{\mu_{real} = \mu_{ideal} + RT\ln\phi}. \tag{17.25}$$

It can be shown that

$$\boxed{\ln\phi = \int_0^p \left(\frac{Z-1}{p}\right) dp} \tag{17.26}$$

where Z is the compressibility factor we saw earlier at the beginning of this class. It will take different forms for different equations of state.

Variations in Helmholtz free energy, preliminaries, $A(T,V)$

I will not dwell on this because we will mostly work with the Gibbs free energy. In addition, you will see this in the next section where we will talk about the fundamental equations of thermodynamics. For now, let's see how the Helmholtz free energy varies with temperature and volume. Recall that by definition

$$A = U - TS$$

so that

$$dA = dU - TdS - SdT.$$

From first and second laws of thermodynamics $dU = TdS - pdV$ (we used this earlier in the Gibbs section)

$$\begin{aligned} dA &= TdS - pdV - TdS - SdT \\ &= -pdV - SdT. \end{aligned}$$

We then have our desired expression

$$\boxed{dA = -pdV - SdT}. \tag{17.27}$$

Through this total differential you can see the change of the Helmholtz free energy with temperature and volume.

Variations of the Helmholtz free energy with temperature, constant volume

At constant volume $dV = 0$. Therefore, we have

$$dA = -SdT$$

or

$$\boxed{\left(\frac{\partial A}{\partial T}\right)_V = -S}. \tag{17.28}$$

As an aside, you can similarly show that for some chemical reaction

$$\boxed{\left(\frac{\partial \Delta A_{rxn}}{\partial T}\right)_V = -\Delta S_{rxn}}. \tag{17.29}$$

The way to show this was first demonstrated when talking about Gibbs free energy differences a few pages ago. I'll let you prove this for yourself.

Back to where we left off. At this point, $A = U - TS$ or $\frac{A-U}{T} = -S$. We have

$$\begin{aligned} \left(\frac{\partial A}{\partial T}\right)_V &= \frac{A-U}{T} \\ \left(\frac{\partial A}{\partial T}\right)_V - \frac{A}{T} &= -\frac{U}{T}. \end{aligned}$$

The term on the left is actually

$$T\left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right]_V$$

and this can be shown explicitly.

"Proof"

$$\begin{aligned} T\left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right]_V &= T\left[A\left(-\frac{1}{T^2}\right)+\frac{1}{T}\left(\frac{\partial A}{\partial T}\right)_V\right] \\ &= -\frac{A}{T}+\left(\frac{\partial A}{\partial T}\right)_V. \end{aligned}$$

Therefore

$$T\left[\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial T}\right)\right]_V = -\frac{U}{T}.$$

Our desired expression is

$$\boxed{\left[\tfrac{\partial}{\partial T}\left(\tfrac{A}{T}\right)\right]_V = -\tfrac{U}{T^2}}. \tag{17.30}$$

This is a no-name equation (maybe there is a name but I didn't bother to dig so deep) that is analogous to the Gibbs-Helmholtz equation derived earlier. The only difference is that we are dealing with the temperature dependence of the Helmholtz free energy.

Alternatively, recognizing -just like we did in the Gibbs section that A and U here are really differences (i.e. ΔA and ΔU), one could write

$$\boxed{\left[\tfrac{\partial}{\partial T}\left(\tfrac{\partial \Delta A}{\partial T}\right)\right]_V = -\tfrac{\Delta U}{T^2}}. \tag{17.31}$$

Again, this will give you the change of the Helmholtz free energy at different temperatures assuming that the internal energy is more or less constant over the temperature range.

Next, just like the Gibbs-Helmholtz equation, we can write this expression a little differently. This is what some authors like to do. Since $d(\frac{1}{T}) = -\frac{1}{T^2}dT$ we can replace $\partial T = -T^2\partial(\frac{1}{T})$. On doing this, we get

$$\boxed{\left(\frac{\partial(\frac{A}{T})}{\partial(\frac{1}{T})}\right)_V = U}. \tag{17.32}$$

Finally, something perhaps more intuitive. Since $A = U - TS$ one can write

$$A(T_1) = U - T_1 S$$

or

$$\Delta A(T_1) = \Delta U - T_1 \Delta S.$$

If we go to a different temperature, we have

$$\Delta A(T_2) = \Delta U(T_1 \to T_2) - T_2 \Delta S(T_1 \to T_2)$$

All we need now is the temperature dependence of both the internal energy and the entropy. But we already know this. Recall that under constant volume conditions

$$\begin{aligned} \left(\frac{\partial U}{\partial T}\right)_V &= C_V \\ \left(\frac{\partial S}{\partial T}\right)_V &= \frac{C_V}{T}. \end{aligned}$$

So the desired expression is therefore

$$\boxed{\Delta A(T_2) = \left[\Delta U(T_1) + \int_{T_1}^{T_2} C_V dT\right] - T_2 \left[\Delta S(T_1) + \int_{T_1}^{T_2} \frac{C_V}{T} dT\right]}. \quad (17.33)$$

Variations of the Helmholtz free energy with volume, constant temperature

From the total differential of $A = f(T, V)$, which is $dA = -pdV - SdT$ we see that under constant temperature conditions

$$dA = -pdV.$$

Alternatively,

$$\boxed{\left(\frac{\partial A}{\partial V}\right)_T = -p}. \quad (17.34)$$

As before, for some chemical reaction, it can likewise be shown (I'll let you do this for yourself) that

$$\boxed{\left(\frac{\partial \Delta A_{rxn}}{\partial V}\right)_T = -\Delta p_{rxn}}. \quad (17.35)$$

Other dependences of either G or A

Both the dependences of the Gibbs and Helmholtz free energies on V and p respectively can be derived. Although p, T are the natural independent variables for G, it is sometimes useful to express G as a function of T and V. The same can be said of the Helmholtz free energy, except in this case as a function of T and p.

The total differentials of $G(V,T)$ and $A(p,T)$ can be shown to have the following forms

$$\boxed{dG = \left[V\left(\frac{\partial p}{\partial T}\right)_V - S\right] dT + \left[V\left(\frac{\partial p}{\partial V}\right)_T\right] dV} \tag{17.36}$$

and

$$\boxed{dA = -\left[p\left(\frac{\partial V}{\partial p}\right)_T\right] dp - \left[p\left(\frac{\partial V}{\partial T}\right)_p + S\right] dT}. \tag{17.37}$$

From these expressions you can find the volume dependence of G and the pressure dependence of A. These expressions, I believe, will be on one of your homeworks so that's why I haven't explicitly worked them out here. Besides, you're curious anyway so I'm sure you would do this on your own anyway.

The Gibbs free energy of formation

Recall that we wanted to predict the spontaneity of a process. We introduced ΔG as a convenient way to do this at constant temperature and pressure. In chemistry, we will want to evaluate ΔG for a reaction. So just like with enthalpy and entropy we will define what is called the Gibbs free energy of formation. ΔG_f^o or ΔG_{298}^o is the change in Gibbs free energy when 1 mole of a compound is formed at 1 bar and 298 K from its elements in their standard states. By definition, ΔG_f^o is zero for pure elements in their standard state. I'm not sure this is important but some more terminology.

- Compounds with a positive ΔG_f^o are called *endergonic*.
- Compounds with a negative ΔG_f^o are called *exogonic*.

Free energy changes in chemical reactions

Now, the variations in Gibbs free energy during chemical reactions can be done a number of ways. Note again, most chemical reactions are conducted under constant pressure. Thus the Gibbs free energy is used here.

Since the free energy is a state function you could take a Hess type of approach. But why bother since there are tables of Gibbs energies of formations for many compounds. So just like in evaluating the enthalpy and entropy changes of a chemical reaction, you just add up the free energy changes on the products side, add up the free energy changes on the reactants side, ensure that you have taken account of the stoichiometry of the reaction and then take the difference, products minus reactants. That's it.

What about the temperature dependence?

As you know, most reactions are not conducted at 298K. As a consequence, we need to know the temperature dependence of the Gibbs free energy. This is where the Gibbs-Helmholtz relation we saw earlier comes into play

$$\begin{aligned}\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right) &= \Delta H \\ d\left(\frac{\Delta G}{T}\right) &= \Delta H d\left(\frac{1}{T}\right)\end{aligned}$$

where we assume ΔH to be temperature independent. This is generally reasonable over a small temperature range. (Note that if you want you could also model the temperature dependence explicitly as we showed earlier.) Our resulting expression is then

$$\boxed{\frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \tag{17.38}$$

from where you can find $\Delta G(T_2)$.

Example

Using data from a table, calculate the standard free energy change at 25^oC and 1 bar for the reaction

$$N_2O_4(g) \rightarrow 2NO_2(g)$$

Ans: (all units kJ/mol)

$$\begin{aligned} N_2O_4(g) &\rightarrow 2NO_2(g) \\ 97.9 &\rightarrow 2(51.3). \end{aligned}$$

The free energy change, products minus reactants is therefore

$$\Delta G^o_{298} = 4.7kJ$$

This process is not spontaneous as you can guess.

A and G and useful non-PV work

We have defined work to be exclusively pV (i.e. pdV) work. However, in more realistic situations there is non-PV work that can be done. Here we show that ΔA and ΔG represent the maximum amount of non-PV work that can be done by a system under constant (T,V) and constant (T,p) conditions respectively.

Useful work, ΔA

Recall that

$$dS \geq \frac{dq_{rev}}{T} = \frac{dU - dw}{T}$$

where dw includes non-pdV work. So it's non-zero here. We could write $dw = -pdV + dw_{other}$ but since $dV = 0$ here let's just write, $dw = dw_{other}$.

$$\begin{aligned} TdS &\geq dU - dw_{other} \\ dU - dw_{other} - TdS &\leq 0. \end{aligned}$$

Since, T is constant, we can add in SdT to the above expression

$$\begin{aligned} dU - dw_{other} - TdS - SdT &\leq 0 \\ dU - d(TS) &\leq dw_{other} \\ d(U - TS) &\leq dw_{other} \end{aligned}$$

giving

$$\boxed{dA \leq dw_{other}}. \tag{17.39}$$

This gives us the maximum amount of non-PV work that can be done by the system under reversible conditions (i.e. when $dA = dw_{other}$). More often than not the less than sign applies (i.e. an irreversible process).

Useful work, ΔG

Start with one of the above equations

$$dU - dw - TdS - SdT \leq 0.$$

Expand using $dw = -pdV + dw_{other}$ to get

$$dU + pdV - dw_{other} - TdS - SdT \leq 0.$$

Since p is constant, we can add in Vdp above

$$\begin{aligned} dU + pdV + Vdp - dw_{other} - TdS - SdT &\leq 0 \\ dU + d(pV) - dw_{other} - d(TS) &\leq 0 \\ d(U + pV) - d(TS) &\leq dw_{other} \\ d(H) - d(TS) &\leq dw_{other} \\ d(H - TS) &\leq dw_{other} \end{aligned}$$

and since $G = H - TS$ we get

$$\boxed{dG \leq dw_{other}}. \tag{17.40}$$

This gives us the maximum amount of useful non-PV work that can be done by the system under reversible conditions (i.e. $dG = dw_{other}$). More often than not, the less than sign applies (i.e. an irreversible process).

Chapter 18

The fundamental equations of thermodynamics

The point of this section is to begin recapping the major equations of thermodynamics. We will first derive what these fundamental equations are and then I will show you a mnemonic that will make life a whole lot easier.

First, I will derive the fundamental equations for U, G, A, H. Namely, important total differentials in each case. Note that these are for single component systems.

The internal energy, U

Use the first and second laws of thermodynamics to derive this. From the first law we have

$$dU = dq + dw$$

where $dw = -pdV$ if only pV work is done and $p = p_{ext}$ for a reversible process. From the second law of thermodynamics, we get

$$dS = \frac{dq}{T}$$

where q is a reversible heat or alternatively

$$dq = TdS.$$

Put both of these expressions together to get

$$\begin{aligned} dU &= dq + dw \\ dU &= TdS - pdV. \end{aligned}$$

The fundamental equation for the internal energy U is therefore

$$\boxed{dU = TdS - pdV}. \tag{18.1}$$

But now recall that we could have written the total derivative of $U(S, V)$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV.$$

By comparison, we see then that

$$\begin{aligned}\left(\frac{\partial U}{\partial S}\right)_V &= T \\ \left(\frac{\partial U}{\partial V}\right)_S &= -p.\end{aligned}$$

We also know from the exactness of the total differential that

$$\begin{aligned}\frac{\partial^2 U}{\partial V \partial S} &= \frac{\partial^2 U}{\partial S \partial V} \\ \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V.\end{aligned}$$

This results in the first of four so called Maxwell relations

$$\boxed{\left(\tfrac{\partial T}{\partial V}\right)_S = -\left(\tfrac{\partial p}{\partial S}\right)_V}. \tag{18.2}$$

The Gibbs free energy, G

$$\begin{aligned}G &= H - TS \\ dG &= dH - TdS - SdT\end{aligned}$$

where $H = U + pV$ and $dH = dU + pdV + Vdp$. Replace this into the above expression

$$dG = dU + pdV + Vdp - TdS - SdT$$

where recall from the last section that $dU = TdS - pdV$. Plug this in also and get

$$\begin{aligned}dG &= TdS - pdV + pdV + Vdp - TdS - SdT \\ &= Vdp - SdT.\end{aligned}$$

We are left with the fundamental equation for the Gibbs free energy

$$\boxed{dG = V\,dp - SdT}. \tag{18.3}$$

Now recall that we could have written the total derivative of $G(p, T)$

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT.$$

By comparison we see then that

$$\begin{aligned}\left(\frac{\partial G}{\partial p}\right)_T &= V \\ \left(\frac{\partial G}{\partial T}\right)_p &= -S.\end{aligned}$$

We also know that from the exactness of the total differential

$$\begin{aligned}\frac{\partial^2 G}{\partial T \partial p} &= \frac{\partial^2 G}{\partial p \partial T} \\ \left(\frac{\partial V}{\partial T}\right)_p &= -\left(\frac{\partial S}{\partial p}\right)_T.\end{aligned}$$

This results in the second of four so called Maxwell relations

$$\boxed{\left(\tfrac{\partial V}{\partial T}\right)_p = -\left(\tfrac{\partial S}{\partial p}\right)_T}. \tag{18.4}$$

The Helmholtz free energy, A

$$\begin{aligned}A &= U - TS \\ dA &= dU - TdS - SdT\end{aligned}$$

where $dU = TdS - pdV$. Thus,

$$\begin{aligned}dA &= TdS - pdV - TdS - SdT \\ &= -pdV - SdT.\end{aligned}$$

We are left with the fundamental equation for the Helmholtz free energy

$$\boxed{dA = -pdV - SdT}. \tag{18.5}$$

Recall now that we could have written the total derivative of $A(V,T)$

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT.$$

By comparison, we see then that

$$\begin{aligned}\left(\frac{\partial A}{\partial V}\right)_T &= -p \\ \left(\frac{\partial A}{\partial T}\right)_V &= -S.\end{aligned}$$

We also know that from the exactness of the total differential

$$\begin{aligned}\frac{\partial^2 A}{\partial T \partial V} &= \frac{\partial^2 A}{\partial V \partial T} \\ \left(\frac{\partial p}{\partial T}\right)_V &= \left(\frac{\partial S}{\partial V}\right)_T.\end{aligned}$$

This results in the third of four so called Maxwell relations

$$\boxed{\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T}. \tag{18.6}$$

The enthalpy, H

$$\begin{aligned}H &= U + pV \\ dH &= dU + pdV + Vdp\end{aligned}$$

where $dU = TdS - pdV$

$$\begin{aligned}dH &= TdS - pdV + pdV + Vdp \\ &= TdS + Vdp.\end{aligned}$$

We are thus left with the fundamental equation for the Enthalpy

$$\boxed{dH = TdS + Vdp}. \tag{18.7}$$

Recall that we could have written the total derivative of $H(S,p)$

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp.$$

By comparison, we see then that

$$\begin{aligned}\left(\frac{\partial H}{\partial S}\right)_p &= T\\ \left(\frac{\partial H}{\partial p}\right)_S &= V.\end{aligned}$$

We also know that from the exactness of the total differential

$$\begin{aligned}\frac{\partial^2 H}{\partial p \partial S} &= \frac{\partial^2 H}{\partial S \partial p}\\ \left(\frac{\partial T}{\partial p}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_p.\end{aligned}$$

This results in the fourth of four so called Maxwell relations

$$\boxed{\left(\tfrac{\partial T}{\partial p}\right)_S = \left(\tfrac{\partial V}{\partial S}\right)_p}. \tag{18.8}$$

The thermodynamic boat

So you're probably wondering how will I ever remember all of these fundamental equations of thermodynamics and their associated Maxwell relations. Well, there is a useful mnemonic I will describe below.

Remember the saying "**Save that ship Gibbs**." Now construct a square as follows

$$\begin{array}{ccc} + & & - \\ S & U & V \\ H & & A \\ p & G & T \end{array}$$

The (+) and (-) sign are for the columns. Note that the functions U, H, A, G, sandwiched by variables on the corners, are the functions whose fundamental equations we will find. Next, to construct a fundamental thermodynamic relation choose one of these functions and take its derivative. Look over to the opposing corners of the cube. For example, for G, we see S and V. Multiply these variables by the opposing diagonal variables in derivative form on either side of the function you have chosen. So for G again we have dp and dT and they are multiplied with V and S respectively. Add the sign by using the column in which these variables in derivative form are located. Since dp is in the positive column we have a plus in front of it. Since dT is in the negative column we have a negative in front of it. So again for G we have

$$dG = Vdp - SdT.$$

Ok, I realize it's hard to visualize what I have just written. It's easier to see it done in real life. Let's do the rest to help you get the trick.

Let's do A. So we call it dA. Next, we look for the variables on the opposing corners of the cube. This time it's S and p. We will multiply S and p with its complementary opposing variable in derivative form on either side of A. So for S we multiply it by dT. So for p we multiply it by dV. Next we need the sign. Since both dV and dT are found in the negative column, the signs will both be negative. Put it all together

$$dA = -pdV - SdT.$$

Let's do H. Call it dH. Next, look for the variables on the opposing corner. They are V and T. Multiply V by its complementary variable in derivative form on the opposing diagonal corner. We get Vdp. Multiply T by its complementary variable in derivative form on the opposing diagonal corner. We get TdS. Now for the signs. Both dS and dp are in the positive column, hence both signs are positive. Put it all together.

$$dH = TdS + Vdp.$$

Finally, let's end with U. Call it dU. Look for the variables on the opposing corner. They are p and T. Multiply T by its complementary diagonal opposing variable in derivative form. We get TdS. Multiply p by its opposing diagonal variable. We get pdV. Next, get the sign by the columns in which dS and dV are located in. For dS we see it's in the positive column, hence we have a positive TdS term. Next, dV is in the negative column so the product, pdV will have a negative in front of it. Put it all together.

$$dU = TdS - pdV.$$

Now you're basically done. If you need Maxwell relations, you can just read it off of the total differentials that you have just derived using this thermodynamic ship mnemonic.

Summary

$$\begin{aligned}
dU &= TdS - pdV \\
\left(\frac{\partial U}{\partial S}\right)_V &= T \\
\left(\frac{\partial U}{\partial V}\right)_S &= -p \\
\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V
\end{aligned}$$

$$\begin{aligned}
dH &= TdS + Vdp \\
\left(\frac{\partial H}{\partial S}\right)_p &= T \\
\left(\frac{\partial H}{\partial p}\right)_S &= V \\
\left(\frac{\partial T}{\partial p}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_p
\end{aligned}$$

$$\begin{aligned}
dA &= -SdT - pdV \\
\left(\frac{\partial A}{\partial T}\right)_V &= -S \\
\left(\frac{\partial A}{\partial V}\right)_T &= -p \\
\left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V
\end{aligned}$$

$$\begin{aligned}
dG &= Vdp - SdT \\
\left(\frac{\partial G}{\partial p}\right)_T &= V \\
\left(\frac{\partial G}{\partial T}\right)_p &= -S \\
\left(\frac{\partial V}{\partial T}\right)_p &= -\left(\frac{\partial S}{\partial p}\right)_T
\end{aligned}$$

Done.

Chapter 19

Application of Free Energy to Phase Transitions

Phase diagram

A phase diagram is a map of the pressures and temperatures at which each phase of a substance is the most stable. The “phase” of a substance is a form of matter uniform in its chemical composition and physical state. Generally speaking, at high temperatures and low pressures we get a gas. At low temperatures and high pressures we get a solid. And somewhere inbetween we get a liquid. **Drawing of phase diagram should go here**

Note the following two points on the phase diagram. They are the triple point and the critical point. **Triple point** The triple point marks the lowest pressure at which a liquid phase of a substance can exist. The critical point is the upper limit. The triple point also represents the temperature and pressure at which three phases of the substance (gas, liquid, and solid) coexist in thermodynamic equilibrium. The triple point of water is at 273.16 K and 0.006 atm.

Critical point This is the upper pressure and temperature at which a liquid exists. Beyond this the liquid becomes another single uniform phase called a supercritical fluid. There is no liquid phase anymore and hence no barrier between the liquid and gas phases (i.e. the distinction between gas and liquid disappears.) Decaffeinated coffee is made this way using supercritical CO_2 to extract caffeine from coffee.

Demo opportunity

There is an online video in youtube that shows the supercritical fluid transition of a substance.

Let's continue

In this next section we will describe the transition of a pure compound from solid to liquid or liquid to vapor or solid to vapor. A key point to remember in what follows is that **for a one component system, at a phase transition the Gibbs free energy or chemical potential is equal in either phase.**

Preliminaries, Chemical potential of a pure substance

Recall that the chemical potential of a *pure* substance is synonymous with its Gibbs free energy. It's just a change of notation.

$$\boxed{\mu = G}. \tag{19.1}$$

In the expression, G is the molar Gibbs free energy (Again, I remind you that what G is here is really a difference in free energy. By convention, one just writes G in these sorts of equations. But it opens up the possibility of people forgetting that there isn't an absolute value of G being discussed.). Now, the place where our notation really changes over from the Gs we're used to -to μ is in mixtures, which we will talk about in the next chapter. We'll see a preview of this when we derive the Clapeyron and Clausius-Clapeyron Equations shortly.

Solid→Liquid

At equilibrium, the free energies of the substance will equal in either phase

$$G(l) = G(s).$$

Thus $\Delta G_{fus} = 0$. But since $G = H - TS$ at a constant temperature, T_m, we get

$$\Delta G_{fus} = \Delta H_{fus} - T_m \Delta S_{fus} = 0$$

or

$$\Delta H_{fus} = T_m \Delta S_{fus}$$

or

$$\boxed{\Delta S_{fus} = \tfrac{\Delta H_{fus}}{T_m}}. \tag{19.2}$$

We have already seen this expression earlier when talking about enthalpies.

Liquid→Gas

Again, the free energies will equal at the phase transition

$$G(l) = G(g).$$

Thus $\Delta G_{vap} = 0$. But since $G = H - TS$ at a constant temperature, T_b, we get

$$\Delta G_{vap} = \Delta H_{vap} - T_b \Delta S_{vap} = 0$$

or

$$\Delta H_{vap} = T_b \Delta S_{vap}$$

or

$$\boxed{\Delta S_{vap} = \tfrac{\Delta H_{vap}}{T_b}}. \tag{19.3}$$

This was seen earlier when talking about enthalpies.

Solid→Gas

Finally, we again have

$$G(s) = G(g).$$

Thus $\Delta G_{sub} = 0$. But since $G = H - TS$ at a constant temperature, T_{sub}, we get

$$\Delta G_{sub} = \Delta H_{sub} - T_{sub} \Delta S_{sub} = 0$$

or

$$\Delta H_{sub} = T_{sub} \Delta S_{sub}$$

or

$$\boxed{\Delta S_{sub} = \tfrac{\Delta H_{sub}}{T_{sub}}}. \tag{19.4}$$

Same comment here as above. We have already seen this expression when first discussing various types of enthalpies.

The solid-liquid boundary, The Clapeyron equation

Now, let's consider the solid/liquid phase transition. We will derive a relationship that allows us to evaluate all of the pressure temperature points along the solid/liquid equilibrium line on a phase diagram. This is called the Clapeyron Equation. Recall that at equilibrium, the Gibbs free energies in either phase will equal. This time, let's switch notation and write

$$\mu_a = \mu_b$$

where $d\mu_a$ (or dG_a if you prefer) is

$$\begin{aligned} d\mu_a &= -S_a dT + V_a dp \\ d\mu_b &= -S_a dT + V_b dp. \end{aligned}$$

Next if $\mu_a = \mu_b$ we have

$$\begin{aligned} d\mu_a &= d\mu_b \\ -S_a dT + V_a dp &= -S_b dT + V_b dp \\ (-S_a + S_b) dT &= (V_b - V_a) dp \\ (S_b - S_a) dT &= (V_b - V_a) dp \\ \Delta S dT &= \Delta V dp. \end{aligned}$$

We rearrange this to get

$$\boxed{\frac{dp}{dT} = \frac{\Delta S}{\Delta V}}. \tag{19.5}$$

If we now recall that $\Delta S = \frac{\Delta H}{T}$ at constant pressure, we get

$$\boxed{\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}}. \tag{19.6}$$

Either expression is called the Clapeyron equation. Note that ΔS, ΔV, and ΔH all represent changes due to the phase transition of a substance. While the Clapeyron equation is an exact expression for the slope of the phase boundary and applies to any phase equilibrium of a pure substance, it is normally associated with the solid-liquid boundary. You will see that modifications to this expression lead to what is referred to as the Clausius-Clapeyron equation, which describes both the liquid-vapor and solid-vapor boundaries. Note also that one can come up with an integrated form of the expression:

$$\boxed{p_2 = p_1 + \frac{\Delta H}{\Delta V} \ln \frac{T_2}{T_1}} \tag{19.7}$$

where we have assumed that ΔH is temperature independent. This is an ok assumption over a limited temperature range. However, if you really wanted you could explicitly model the temperature dependence of ΔH through the power series expansion in T as we showed earlier.

So at the solid-liquid boundary we have

$$\boxed{\frac{dp}{dT} = \frac{\Delta H_{fus}}{T_m \Delta V_{fus}}} \tag{19.8}$$

where $\Delta S_{fus} = \frac{\Delta H_{fus}}{T}$ at constant pressure. Now, in most cases in the transition from solid to liquid the density of the material changes so that ΔV_{fus} is positive. As a consequence, the slope predicted by the Clapeyron equation will often be positive. It also says that **melting temperatures, T_m, generally increase with increasing pressure.**

But in some very special cases, on going from solid to liquid, ΔV will be negative. Ice is a common example of this (think of why you never keep Coke cans in the freezer, the stuff expands and blows up.) As a consequence, the slope predicted by the Clapeyron equation will sometimes be negative. This says that for special cases the melting temperature, T_m, decreases with increasing pressure.

Example

The melting point of Na is 97.8^oC at 1 atm. The densities of solid Na and liquid Na are

$$\begin{aligned} Na(s)\rho &= 0.929g/cm^3 \\ Na(l)\rho &= 0.952g/cm^3. \end{aligned}$$

Also $\Delta H_{fus} = 3$ kJ/mol. Calculate the melting point of Na at p=120 atm.

Ans: Employ the Clapeyron equation.

$$\begin{aligned} \frac{dp}{dT} &= \frac{\Delta H_{fus}}{T\Delta V} \\ \frac{dp}{dT} &= \frac{(3kJ/mol)}{(370.95K)(-0.6cm^3/mol)}. \end{aligned}$$

As an approximation, $dp \to \Delta p$ and $dT \to \Delta T$.

$$
\begin{aligned}
\frac{(120 - 1atm)}{(T_2 - 370.95K)} &= \frac{(3kJ/mol)}{(370.95K)(-0.6cm^3/mol)} \\
\frac{(119atm)(1.01 \times 10^5 Pa/atm)}{(T_2 - 370.95K)} &= \frac{-(3000J/mol)}{(370.95K)(0.6cm^3/mol)(1 \times 10^{-6} m^3/cm^3)} \\
\frac{1.2 \times 10^7 Pa}{T_2 - 370.95K} &= \frac{-3000kg \cdot m^2/s^2}{370.95K(0.6)(1 \times 10^{-6})m^3} \\
\frac{1.2 \times 10^7 Pa}{T_2 - 370.95K} &= -1.34 \times 10^7 Pa/K \\
T_2 - 370.95K &= \frac{-1.2 \times 10^7}{1.34 \times 10^7} = 0.89K
\end{aligned}
$$

We are left with the final answer

$$T_2 = 370.95 - 0.89K = 370.06K(96.9C).$$

For fun, why don't you integrate the Clapeyron Equation and compare the exact answer to this.

The liquid-vapor and solid-vapor boundaries, The Clausius-Clapeyron equation

While the Clapeyron equation is, in principle, applicable to all phase changes in single component systems, the equation can be recast into a more useful form when one of the phases is a gas. The major difference here is that ΔV will be huge because we are dealing with a gas. Recall that the volume occupied by a gas is significantly larger than that of a solid or a liquid.

Starting with the Clapeyron equation, replace ΔV with $V(g)$, the volume of a gas, since $V(l)$ and $V(s)$ are much smaller and $V(g)$ dominates.

$$
\begin{aligned}
\frac{dp}{dT} &= \frac{\Delta H_{vap}}{T\Delta V} \\
\frac{dp}{dT} &\simeq \frac{\Delta H_{vap}}{TV(g)}.
\end{aligned}
$$

Next, assume the gas is ideal so that $V(g) = \frac{RT}{p}(n = 1)$. This volume is now the molar volume and some authors will denote it V_m. Finally assume that ΔH_{vap} is constant with temperature. Replace all of this into the above

Clapeyron equation to get

$$\begin{aligned}
\frac{dp}{dT} &\simeq \frac{\Delta H_{vap}p}{T(RT)} \\
\frac{dp}{p} &\simeq \frac{\Delta H_{vap}}{R}\frac{dT}{T^2} \\
\ln p|_{p_1}^{p_2} &\simeq \frac{\Delta H_{vap}}{R}\left.\frac{-1}{T}\right|_{T_1}^{T_2} \\
\ln\frac{p_2}{p_1} &\simeq -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right).
\end{aligned}$$

The desired Clausius-Clapeyron expression is then

$$\boxed{ln\frac{p_2}{p_1} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} \tag{19.9}$$

and relates the pressure/temperature points along the condensed phase/gas phase equilibrium line of a phase diagram. Basically, if you have a boiling/sublimation T and p for a given substance, you can find its new boiling/sublimation temperature at another pressure or conversely its new boiling/sublimation pressure at another temperature.

Example

The normal boiling point of benzene is 80.1^{o}C and the enthalpy of vaporization is $\Delta H_{vap} = 30.8kJ/mol$. Calculate the boiling point of benzene at 100 torr.

Ans:

$$\begin{aligned}
\ln\frac{100torr}{760torr} &= \frac{30.8kJ/mol}{8.314J/molK}\left(\frac{1}{353.25K}-\frac{1}{T_2}\right) \\
\ln(0.132) &= \frac{30800J/mol}{8.314J/molK}\left(\frac{1}{353.25K}-\frac{1}{T_2}\right) \\
-2.025 &= 3704.6\left(\frac{1}{353.25}-\frac{1}{T_2}\right) \\
-5.47\times 10^{-4} &= \left(\frac{1}{353.25}-\frac{1}{T_2}\right) \\
-5.45\times 10^{-4}-\frac{1}{353.25} &= -\frac{1}{T_2}
\end{aligned}$$

leading to our answer

$$T_2 = 296.2K(23.05^oC).$$

This is benzene's new boiling point at 100 torr.

An alternative Clausius-Clapeyron expression

Alternatively, we could have taken the indefinite integral of

$$\frac{dp}{p} = \frac{\Delta H_{vap}}{R}\frac{dT}{T^2}$$

to get

$$\boxed{\frac{d\ln p}{dT} = \frac{\Delta H}{RT^2}} \tag{19.10}$$

giving

$$\ln p = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + const.$$

This is also sometimes called the Clausius-Clapeyron equation. Even more progress can be made if we consider $p = 1bar$ and T_b at 1 bar. Then this expression becomes

$$\ln(1) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_b}\right) + const = 0.$$

Therefore

$$const = \frac{\Delta H_{vap}}{RT_b} = \frac{\Delta S_{vap}}{R}.$$

Thus, another way to write the Clausius-Clapeyron equation is

$$\boxed{\ln p = \frac{\Delta S_{vap}}{R} - \frac{\Delta H_{vap}}{RT}}. \tag{19.11}$$

From this equation you can find the entropy of vaporization by plotting $\ln p$ vs $\frac{1}{T}$ and looking at the intercept. It turns out that the entropy of vaporization is similar for many liquids and is about 85 J/mol

$$\boxed{\Delta S_{vap} = 85J/molK}. \tag{19.12}$$

This empirical finding is referred to as **Trouton's rule** named after this guy Trouton whose Chem. Ed. article we saw earlier. At the end of the day, the Clausius-Clapeyron equation predicts a linear relationship between $\frac{1}{T_b}$ and p.

Now at the solid-vapor boundary the only difference is that ΔH_{vap} is replaced with ΔH_{sub}. Otherwise, it is the same expression as for the liquid-vapor boundary.

Recap

Let's recap both the Clausius and Clausius-Clapeyron Equations with one last example.

Example

Many of the highest mountains in the world are in excess of 25,000 feet. At these altitudes $p = 250$ torr. Calculate the freezing point and boiling point of water at this pressure.

Given:

- the density of ice is: $\rho_{ice} = 0.92 g/cm^3$
- the density of water is: $\rho_{H20} = 1.00 g/cm^3$
- $\Delta H_{fus} = 6.01 kJ/mol$
- $\Delta H_{vap} = 40.7 kJ/mol$

Ans: Use the Clapeyron equation for fusion and the Clausius-Clapeyron equation for vaporization. The Clapeyron equation gives

$$\frac{dp}{dT} = \frac{\Delta H_{fus}}{T_m \Delta V_{fus}}.$$

Making the approximation $dp \rightarrow \Delta p$ and $dT \rightarrow \Delta T$ we get

$$\frac{(250 torr - 760 torr)}{T_2 - 273.15K} = \frac{(6.01 kJ/mol)}{(273.15K)(-1.565 cm^3)}.$$

Convert torr to Pa, convert J to kgm^2/s^2 and convert cm^3 to m^3. This gives

$$\begin{aligned} -\frac{67993.2 Pa}{T_2 - 273.15K} &= \frac{(6000 kgm^2/s^2)}{(273.15K)(-1.565 \times 10^{-6} m^3)} \\ -\frac{67993.2 Pa}{T_2 - 273.15K} &= -1.4 \times 10^7 Pa/K \end{aligned}$$

and yields

$$\Delta T = 0.005K$$

as the freezing point temperature change on the mountain.

Next, use the Clausius-Clapeyron equation to find the solution to the boiling point change.

$$\begin{aligned}
\ln\frac{p_2}{p_1} &= \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\\
\ln\frac{250}{760} &= \frac{40700}{8.314}\left(\frac{1}{373.15}-\frac{1}{T_2}\right)\\
-1.112 &= 4895.4\left(\frac{1}{373.15}-\frac{1}{T_2}\right)\\
-2.3\times 10^{-4} &= \left(\frac{1}{373.15}-\frac{1}{T_2}\right)\\
-2.3\times 10^{-4}-\frac{1}{373.15} &= -\frac{1}{T_2}\\
\frac{1}{T_2} &= 0.0029098.
\end{aligned}$$

Our desired answer is

$$T_2 = 343.7K(70.5C).$$

We see that the boiling point is lower on a mountain. From this example, you see that the melting point difference is negligible but that the boiling point change is significant.

Demo opportunity A vacuum boiling demo could go here provided I have this instrument.

Chapter 20

Mixtures

Chemistry deals with mixtures that potentially react. As a first step to describe the thermodynamics of these systems, we will simply deal with binary mixtures that do not react. Note that up to now we have primarily been working with closed systems of constant composition. For example, our system is a gas and does some expansion whereupon we find the associated changes in free energy as well as other thermodynamic quantities. In general, though, these thermodynamic state functions actually depend upon the amount of stuff one has, which is especially important in the case of a system with variable composition (i.e. mixtures and reactions as you will see in the equilibrium section later).

Preliminaries, partial molar properties

First, an introduction into what are called partial molar properties.

Partial molar volume

The partial molar volume of a substance in a mixture is defined as

$$V_i = \left(\frac{\partial V}{\partial n_i}\right)$$

where the subscript i just refers to a species of interest. For a 2 component binary mixture of species A and B, then, if the amounts of A and B are varied, the total volume of the mixture changes by

$$dV = \left(\frac{\partial V}{\partial n_a}\right)_{p,T,n_b} dn_a + \left(\frac{\partial V}{\partial n_b}\right)_{p,T,n_a} dn_b.$$

The corresponding total volume is therefore

$$V = \left(\frac{\partial V}{\partial n_a}\right) n_a + \left(\frac{\partial V}{\partial n_b}\right) n_b$$

where n_a and n_b are the moles of A and B respectively.

Partial molar Gibbs free energy

Recall that the chemical potential in the case of a single component is the same as the Gibbs free energy ($\mu = G$) (actually it's the molar Gibbs free energy to be absolutely correct). In the case of mixtures,

$$\boxed{\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_j}}. \tag{20.1}$$

The total Gibbs free energy of a binary mixture of species A and B at constant T and p is then

$$\boxed{dG = \mu_a dn_a + \mu_b dn_b} \tag{20.2}$$

such that

$$\boxed{G = \mu_a n_a + \mu_b n_b} \tag{20.3}$$

where n_a and n_b are the moles of A and B present in the mixture.

Next, to complicate things, recall that in general, the Gibbs free energy will also depend on the pressure and temperature (you've already seen this in previous sections). As a consequence, we write

$$dG = V dp - S dT + \mu_a dn_a + \mu_b dn_b$$

for our binary mixture. Of course, if there are more than two components you keep adding the little chemical potential terms at the end where at constant pressure and temperature, this simplifies back to

$$dG = \mu_a dn_a + \mu_b dn_b.$$

The Gibbs free energy, G

In general, we have

$$\boxed{dG = V dp - S dT + \textstyle\sum_i \mu_i dn_i}. \tag{20.4}$$

This may also be written as

$$\boxed{dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} dn_i} \tag{20.5}$$

where under constant T and p conditions the equation reduces to

$$\boxed{dG = \sum_i \mu_i dn_i}. \tag{20.6}$$

The dependencies of other thermodynamic functions

Consider the dependencies of other thermodynamic functions with composition. fsWe will use the following (previously) derived relationships

$$\begin{aligned} G &= A + pV \\ G &= H - TS \\ H &= U + pV. \end{aligned}$$

The Helmholtz free energy, A

Since

$$dG = Vdp - SdT + \sum_i \mu_i dn_i$$

and

$$A = G - pV$$

we get

$$\begin{aligned} dA &= dG - pdV - Vdp \\ &= \left(-SdT + Vdp + \sum_i \mu_i dn_i\right) - pdV - Vdp \\ &= -SdT - pdV + \sum_i \mu_i dn_i \end{aligned}$$

or that

$$\boxed{dA = -SdT - pdV + \sum_i \mu_i dn_i}. \tag{20.7}$$

This may also be written as

$$\boxed{dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV + \sum_i \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j}}. \tag{20.8}$$

Furthermore, we can see that an alternative expression for the chemical potential is

$$\boxed{\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j}}. \tag{20.9}$$

The enthalpy, H

Since

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i$$

and

$$G = H - TS$$

we get

$$\begin{aligned} dH &= dG + TdS + SdT \\ &= \left(-SdT + Vdp + \sum_i \mu_i dn_i\right) + TdS + SdT \\ &= Vdp + TdS + \sum_i \mu_i dn_i \end{aligned}$$

or that

$$\boxed{dH = Vdp + TdS + \sum_i \mu_i dn_i}. \tag{20.10}$$

This may also be written as

$$\boxed{dH = \left(\frac{\partial H}{\partial p}\right)_S dp + \left(\frac{\partial H}{\partial S}\right)_p dS + \sum_i \left(\frac{\partial H}{\partial n_i}\right)_{T,S,n_j}}. \tag{20.11}$$

Furthermore, we see that an alternative expression for the chemical potential is

$$\boxed{\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_j}}. \tag{20.12}$$

The internal energy, U

Since

$$dH = Vdp + TdS + \sum_i \mu_i dn_i$$

and

$$U = H - pV$$

we get

$$\begin{aligned} dU &= dH - pdV - Vdp \\ &= \left(Vdp + TdS + \sum_i \mu_i dn_i\right) - pdV - Vdp \end{aligned}$$

or that

$$\boxed{dU = TdS - pdV + \textstyle\sum_i \mu_i dn_i}. \tag{20.13}$$

This may also be written as

$$\boxed{dU = \left(\tfrac{\partial U}{\partial S}\right)_V dS + \left(\tfrac{\partial U}{\partial V}\right)_S dV + \textstyle\sum_i \left(\tfrac{\partial U}{\partial n_i}\right)_{S,V,n_j}}. \tag{20.14}$$

Furthermore, we see that an alternative expression for the chemical potential is

$$\boxed{\mu_i = \left(\tfrac{\partial U}{\partial n_i}\right)_{S,V,n_j}} \tag{20.15}$$

More games

Since $G = H - TS$ we get

$$\begin{aligned} G &= H - TS \\ G &= (U + pV) - TS \\ U &= G - pV + TS \\ dU &= dG - pdV - Vdp + TdS + SdT \end{aligned}$$

where recall from above that in general $dG = Vdp - SdT + \mu_a dn_a + \mu_b dn_b$ for a binary mixture. Plug this into the above expression to get

$$\begin{aligned} dU &= Vdp - SdT + \mu_a dn_a + \mu_b dn_b - pdV - Vdp + TdS + SdT \\ &= -pdV + TdS + \mu_a dn_a + \mu_b dn_b. \end{aligned}$$

This again leads to

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j}$$

The Gibbs-Duhem equation, a relationship between partial molar properties

Recall that under constant temperature and pressure conditions for a binary mixture

$$G = \mu_a n_a + \mu_b n_b.$$

But note now that you could write

$$dG = \mu_a dn_a + n_a d\mu_a + \mu_b dn_b + n_b d\mu_b$$

whereas we previously showed that under constant T and p conditions

$$dG = \mu_a dn_a + \mu_b dn_b.$$

Thus, for these two equations to equal

$$\boxed{n_a d\mu_a + n_b d\mu_b = 0}. \tag{20.16}$$

This relationship is referred to as the Gibbs-Duhem equation. More generally

$$\boxed{\textstyle\sum_i n_i d\mu_i = 0} \tag{20.17}$$

and its significance is that the chemical potential of one component of a mixture cannot change independently of the chemical potentials of the other components.

So in our binary mixture, if one chemical potential increases, the other must decrease.

$$\begin{aligned} n_a d\mu_a + n_b d\mu_b &= 0 \\ n_b d\mu_b &= -n_a d\mu_a \\ d\mu_b &= -\frac{n_a}{n_b} d\mu_a. \end{aligned}$$

The Gibbs-Duhem equation is general. Note that one could also write $n_{tot} = n_A + n_B$ with $\chi_A = \frac{n_A}{n_{tot}}$ and $\chi_B = \frac{n_B}{n_{tot}}$. Thus

$$d\mu_b = -\frac{\chi_a}{\chi_b} d\mu_a$$

where χ_a and χ_b are the mole fractions of A and B.

Mixing of ideal gases

Let's now move to mixing problems. The changes in Gibbs free energy as well as internal energy, enthalpy, entropy, etc... can be calculated on the basis of the following Gedanken experiment.

Picture a cylinder where you have two gases, call them A and B that are separated by two semipermeable membranes (one is permeable to A only, the other is permeable to B only). Gas A is on the left. Gas B is on the right. The two semipermeable membranes are just about touching. The external pressures on the right and the left are initially at the exact same pressure as gases A and B. So at this point nothing moves.

Next, the mixing is carried out reversibly (and also isothermally) by reducing the external pressure on either side by an infinitesimally small amount. Gases A and B then initiate a mixing by slowly moving the semipermeable barriers apart until the volumes have doubled.

The work, heat and internal energy of this mixing process

The work done during the expansion is the sum of the work incurred by both moving semipermeable barriers.

$$\begin{aligned}
w_{mix} &= w_A + w_B \\
&= -\int_{V_A}^{V_A+V_B} p_A dV - \int_{V_B}^{V_A+V_B} p_B dV \\
&= -\int_{V_A}^{V_A+V_B} \frac{n_A RT}{V} dV - \int_{V_B}^{V_A+V_B} \frac{n_B RT}{V} dV \\
&= -n_A RT \ln \frac{V_A+V_B}{V_A} - n_B RT \ln \frac{V_A+V_B}{V_B} \\
&= n_A RT \ln \frac{V_A}{V_A+V_B} + n_B RT \ln \frac{V_B}{V_A+V_B}.
\end{aligned}$$

Note that the volumes are proportional to the number of moles of each gas (verify this for yourself). Therefore, we can also write

$$\begin{aligned}
w_{mix} &= n_A RT \ln \frac{n_A}{n_A+n_B} + n_B RT \ln \frac{n_B}{n_A+n_B} \\
&= n_A RT \ln \frac{n_A}{n_{tot}} + n_B RT \ln \frac{n_B}{n_{tot}} \\
&= n_A RT \ln \chi_A + n_B RT \ln \chi_B.
\end{aligned}$$

This leads to our final expression for the work involved during mixing

$$\boxed{w_{mix} = n_{tot} RT (\chi_A \ln \chi_A + \chi_B \ln \chi_B)}. \tag{20.18}$$

Since the mixing is isothermal and both gases are ideal

$$\boxed{\Delta U_{mix} = 0} \tag{20.19}$$

and

$$\boxed{\Delta H_{mix} = 0}. \tag{20.20}$$

Then by the first law of thermodynamics we know that

$$q_{mix} = -w_{mix}$$

giving

$$\boxed{q_{mix} = -n_{tot}RT(\chi_A \ln \chi_A + \chi_B \ln \chi_B)}. \tag{20.21}$$

The Gibbs free energy of mixing

We are now interested in the Gibbs free energy of mixing. There are a number of ways to evaluate this. The easiest is to recall that when the process is isothermal and reversible the entropy change is basically the heat of the reversible process over the temperature. Then once you have ΔS_{mix} you can get ΔG from $\Delta G_{mix} = \Delta H_{mis} - T\Delta S_{mix}$. We will call this case 1. Alternatively, there is a more advanced way to do this. It entails knowing what the chemical potential of a substance is once mixed. One then subtracts the original chemical potential of the substance from this value to get the difference.

Case 1

$$\begin{aligned} \Delta S_{mix} &= \frac{q_{rev}}{T} \\ &= \frac{q_{mix}}{T} \\ &= \frac{-nRT(\chi_A \ln \chi_A + \chi_B \ln \chi_B)}{T}. \end{aligned}$$

Then

$$\boxed{\Delta S_{mix} = -nR(\chi_A \ln \chi_A + \chi_B \ln \chi_B)}. \tag{20.22}$$

To get ΔG_{mix} we know that $\Delta H_{mix} = 0$. We therefore employ

$$\begin{aligned}\Delta G &= \Delta H_{mix} - T\Delta S_{mix} \\ &= nRT(\chi_A \ln \chi_A + \chi_B \ln \chi_B)\end{aligned}$$

to find

$$\boxed{\Delta G_{mix} = nRT(\chi_A \ln \chi_A + \chi_B \ln \chi_B)}. \tag{20.23}$$

Case 2

Now this case foreshadows something we will demonstrate in an upcoming section. If you knew what the chemical potential of the substance was after it got mixed, you could subtract from this the original chemical potential when unmixed to get the energy change on mixing. We already know what the unmixed free energy change is. All we need is an expression for the chemical potential of the substance once mixed. We will derive this shortly. For now, just watch.

First, for a two component system

$$G = n_a\mu_a + n_b\mu_b$$

where, for an ideal gas, the unmixed chemical potential is

$$\mu = \mu^o + RT \ln \frac{p}{p^o}$$

with μ^o the chemical potential at 1 bar and 25^o C and p is the pressure of the gas divided by p^o which is 1 bar.

This is derived in an earlier discussion within the free energy chapter. Starting with

$$dG = V dp - SdT$$

we now assume constant temperature conditions ($dT = 0$) to get

$$dG = V dp.$$

Since the gas is ideal, $V = \frac{RT}{p}$ (we are dealing with molar volumes here so $n = 1$).

$$\begin{aligned}dG &= \frac{RT}{p} dp \\ \Delta G &= RT \ln \frac{p_2}{p_1} \\ G_2 &= G_1 + RT \ln \frac{p_2}{p_1}\end{aligned}$$

and instead of using G we invoke μ. Thus, let $G_2 \to \mu$, $G_1 \to \mu_o$, $p_2 \to p$, and $p_1 \to p_o$.

Here is the part which we haven't talked about yet. **What is the chemical potential of a gas once mixed?** Well, the chemical potential of the gas once mixed is basically the same expression as before except with p is replaced by p_i, the gas' partial pressure in the mixture. The chemical potential of the mixed gas can then be written as

$$\mu = \mu^o + RT \ln \frac{p_i}{p^o}.$$

Back to our problem. Before mixing we had

$$G = n_a \left[\mu_a^o + RT \ln \frac{p}{p_o} \right] + n_b \left[\mu_b^o + RT \ln \frac{p}{p_o} \right]$$

for the 2 gases separated with p the same in either container.

$$G_{before} = n_a \left[\mu_a^o + RT \ln \frac{p}{p^o} \right] + n_b \left[\mu_b^o + RT \ln \frac{p}{p^o} \right].$$

Now, the two gases are allowed to mix, doubling the volume.
So after mixing we have $p_a + p_b = p$ where p_a and p_b are the partial pressures of A and B. The expression for G after mixing therefore becomes

$$G_{after} = n_a \left[\mu_a^o + RT \ln \frac{p_a}{p^o} \right] + n_b \left[\mu_b^o + RT \ln \frac{p_b}{p^o} \right].$$

We can now find out what the change in free energy is on mixing the two ideal gases

$$\begin{aligned}
\Delta G_{mix} &= G_{after} - G_{before} \\
&= n_a \left[\mu_a^o + RT \ln \frac{p_a}{p^o} \right] + n_b \left[\mu_b^o + RT \ln \frac{p_b}{p^o} \right] \\
&- n_a \left[\mu_a^o + RT \ln \frac{p}{p^o} \right] - n_b \left[\mu_b^o + RT \ln \frac{p}{p^o} \right] \\
&= n_a \left[RT \ln p_a - RT \ln p \right] + n_b \left[RT \ln p_b - RT \ln p \right] \\
&= n_a \left[RT \ln \frac{p_a}{p} \right] + n_b \left[RT \ln \frac{p_b}{p} \right] \\
&= n_a RT \ln \frac{p_a}{p} + n_b RT \ln \frac{p_b}{p}.
\end{aligned}$$

If we replace all pressures by mole fractions we get

$$\Delta G_{mix} = \chi_a n_{tot} RT \ln \chi_a + \chi_b n_{tot} RT \ln \chi_b$$

leading to

$$\boxed{\Delta G_{mix} = nRT(\chi_a \ln \chi_a + \chi_b \ln \chi_b)}. \tag{20.24}$$

Notice that since $\chi_{a,b} < 1$ both ln terms will be less than zero. Thus $\Delta G_{mix} < 0$ is negative. This confirms that the mixing of ideal gases is spontaneous.

Example

Calculate the Gibbs free energy of mixing. Note that this is being worked out using the case 2 approach.

A container is divided into 2 equal compartments. One contains 3 mol of H_2 at 25^oC. The other contains 1 mol of N_2 at 25^oC. Calculate the ΔG of mixing.

Ans:

$$\begin{aligned} G_{before} &= n_a[\mu_a^o + RT\ln p] + n_b[\mu_b^o + RT\ln 3p] \\ &= (1)[\mu_a^o + RT\ln p] + (3)[\mu_b^o + RT\ln 3p]. \end{aligned}$$

After mixing, the volume doubles so that all pressures initially drop by half. We are assuming ideal gas behavior.

$$\begin{aligned} p &\rightarrow \frac{1}{2}p \\ 3p &\rightarrow \frac{3}{2}p. \end{aligned}$$

Thus,

$$G_{after} = (1)\left[\mu_a^o + RT\ln\frac{p}{2}\right] + (3)\left[\mu_b^o + RT\ln\frac{3p}{2}\right].$$

So the difference, final minus initial, is

$$\begin{aligned} \Delta G_{mix} &= RT\ln\frac{p/2}{p} + 3RT\ln\frac{3p/2}{3p} \\ &= RT\ln\frac{1}{2} + 3RT\ln\frac{1}{2} \\ &= -RT\ln 2 - 3RT\ln 2 \\ &= -4RT\ln 2 \\ &= -4(8.314J/molK)(298.15)\ln(2) = -6.87\times 10^3 J. \end{aligned}$$

The answer is

$$\Delta G_{mix} = -6.87kJ.$$

The value is negative so the mixing is spontaneous.

The final chemical potential of a substance in a mixture

We just saw in the prior example that the chemical potential of a gas once mixed has the form

$$\boxed{\mu = \mu^o + RT\ln \tfrac{p_i}{p^o}} \tag{20.25}$$

where p_i is the partial pressure of the gas in the mixture.

In this section, let's just derive this result more formally. Start with the fact that at constant temperature and pressure for a binary system

$$G = n_A\mu_A + n_B\mu_B.$$

Then realize that the free energy of mixing is just the difference of G after minus that before

$$\Delta G_{mix} = G_{mix} - G_{pure}$$

where

$$\begin{aligned} G_{mix} &= n_A\mu_A + n_B\mu_B \\ G_{pure} &= n_A\mu_{A,pure} + n_B\mu_{B,pure}. \end{aligned}$$

Next, I previously showed you that for a pure single component substance (a gas here) that the chemical potential could be written as

$$\mu_{i,pure} = \mu_i^o + RT\ln\frac{p}{p^o}.$$

Let's replace this into our ΔG_{mix} expression above.

$$\Delta G_{mix} = n_A\mu_A + n_B\mu_B - n_A\left(\mu_A^o + RT\ln\frac{p}{p^o}\right) - n_B\left(\mu_B^o + RT\ln\frac{p}{p^o}\right).$$

At this point, invoke $\Delta G_{mix} = n_ART\ln\chi_A + n_BRT\ln\chi_B$ which we derived separately through the case 1 approach. We incorporate this into the LHS of the above equality to get

$$\begin{aligned} n_ART\ln\chi_A + n_BRT\ln\chi_B &= n_A\mu_A + n_B\mu_B - n_A\left(\mu_A^o + RT\ln\frac{p}{p^o}\right) \\ &- n_B\left(\mu_B^o + RT\ln\frac{p}{p^o}\right) \\ n_A(RT\ln\chi_A) + n_B(RT\ln\chi_B) &= n_A\left(\mu_A - \mu_A^o - RT\ln\frac{p}{p^o}\right) \\ &+ n_B\left(\mu_B - \mu_B^o - RT\ln\frac{p}{p^o}\right) \end{aligned}$$

Since the coefficients of n_A and n_B must equal on both sides of the equation, we are left with

$$\begin{aligned} RT\ln\chi_A &= \mu_A - \mu_A^o - RT\ln\frac{p}{p^o} \\ RT\ln\chi_B &= \mu_B - \mu_B^o - RT\ln\frac{p}{p^o}. \end{aligned}$$

Solve for μ_A and μ_B. We want these because they are the chemical potentials of both substances after being mixed.

$$\begin{aligned} \mu_A &= RT\ln\chi_A + \mu_A^o + RT\ln\frac{p}{p^o} \\ \mu_B &= RT\ln\chi_B + \mu_B^o + RT\ln\frac{p}{p^o}. \end{aligned}$$

Consolidate terms to get

$$\begin{aligned} \mu_A &= \mu_A^o + RT\ln\frac{\chi_A p}{p^o} \\ \mu_B &= \mu_B^o + RT\ln\frac{\chi_B p}{p^o} \end{aligned}$$

where we know that the partial pressures are $p_A = \chi_A p$ and $p_B = \chi_B p$. This then yields our desired expressions

$$\begin{aligned} \mu_A &= \mu_A^o + RT\ln\frac{p_A}{p^o} \\ \mu_B &= \mu_B^o + RT\ln\frac{p_B}{p^o}. \end{aligned}$$

So in general, the chemical potential of a substance (a gas here although you will see a more general case next when we talk about liquids) once mixed can be written as

$$\boxed{\mu_i = \mu_i^o + RT\ln\tfrac{p_i}{p^o}}. \tag{20.26}$$

Other thermodynamic mixing functions involving ideal gases

Since $\left(\frac{\partial G}{\partial T}\right)_{p,n_j} = -S$ it follows from

$$\Delta G_{mix} = nRT(\chi_a\ln\chi_a + \chi_b\ln\chi_b)$$

that

$$\boxed{\Delta S_{mix} = -nR(\chi_a\ln\chi_a + \chi_b\ln\chi_b)}. \tag{20.27}$$

Notice that both $\ln \chi_a$ and $\ln \chi_b$ are less than zero. Hence ΔS_{mix} is positive and the process is favored. The system is more disordered. Alternatively, you could have calculated this from

$$\Delta S_{mix} = \frac{q_{mix}}{T}$$

since the process was isothermal and was done reversibly, hence $q_{mix} = q_{rev}$.

Next, from

$$\begin{aligned}\Delta G_{mix} &= \Delta H_{mix} - T\Delta S_{mix} \\ \Delta G_{mix} + T\Delta S_{mix} &= \Delta H_{mix}.\end{aligned}$$

From our previous results we then see that

$$\boxed{\Delta H_{mix} = 0}. \tag{20.28}$$

Alternatively, note that H is only temperature dependent for ideal gases and that the process was isothermal. Hence, we could have (and actually did) immediately say that $\Delta H_{mix} = 0$.

Next, from

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

we get

$$\boxed{\Delta V_{mix} = 0}, \tag{20.29}$$

showing that there is no volume change on mixing ideal gases (i.e. the volumes are additive).

The mixing of ideal liquids

Let's do liquids now. Consider a binary mixture again for simplicity. The derived results will be general. Also assume constant temperature and pressure conditions so that

$$G = n_a\mu_a + n_b\mu_b$$

where

$$\boxed{\mu_i = \mu_i^o + RT\ln a_i}. \tag{20.30}$$

Here a is called the "activity" and the above expression is for the chemical potential of the substance once mixed.

So what is this activity business? Let's illustrate. Consider the vapor-liquid equilibrium of a single substance. We have seen that at equilibrium the chemical potentials are the same in either phase

$$\mu(g) = \mu(l).$$

We know from a previous section that for gases in a mixture

$$\mu_i(g) = \mu_i^o(g) + RT \ln \frac{p_i}{p^o}$$

where p_i is the gas' partial pressure, p^o is 1 bar, and μ_i^o is the chemical potential of the gas in its standard state. I'm now asserting that a similar expression holds for liquids using this so-called activity.

$$\mu_i(l) = \mu_i^o(l) + RT \ln a_i.$$

This results in the following equality at equilibrium

$$\begin{array}{rcl} \mu(g) & = & \mu(l) \\ \mu_i^o(g) + RT \ln \frac{p_i}{p^o} & = & \mu_i^o(l) + RT \ln a_i \end{array}$$

This equation can be applied to a pure liquid where the activity is **defined** as $1(a = 1)$

$$\mu_i^o(g) + RT \ln \frac{p_i^*}{p^o} = \mu_i^o(l).$$

The asterisk signifies that this particular pressure is for a pure substance and p^o is the standard pressure of 1 bar. Thus p_i^* is the pure liquid vapor pressure.

Subtract one equation from the other to get

$$\begin{array}{rcl} RT \ln \frac{p_i}{p_o} - RT \ln \frac{p_i^*}{p^o} & = & RT \ln a_i \\ RT \ln p_i - RT \ln p^o - RT \ln p_i^* + RT \ln p^o & = & RT \ln a_i \\ RT \ln \frac{p_i}{p_i^*} & = & RT \ln a_i. \end{array}$$

Therefore, one finds that the activity is

$$\boxed{a_i = \frac{p_i}{p_i^*}}. \tag{20.31}$$

This ratio also equals χ_i

$$\boxed{a_i = \frac{p_i}{p_i^*} = \chi_i}. \tag{20.32}$$

The last equivalence relating the partial pressure to the mole fraction is basically called Raoult's Law and will be discussed below (**the ratio of the partial pressure to the pure vapor pressure is equivalent to the mole fraction of a given component** or alternatively that the activity is the mole fraction of a substance in a mixture). For now just hold this to be true. You will see more about activities shortly in the equilibrium chapter.

Now back to the point before we went on this tangent about activities. In a binary mixture of liquids at constant T and p,

$$G = n_a\mu_a + n_b\mu_b$$

where

$$\begin{aligned}\mu_i &= \mu_i^o + RT\ln a_i \\ &= \mu_i^o + RT\ln\chi_i.\end{aligned}$$

So before mixing (constant T, p) we have

$$G_{before} = n_a\mu_a^o + n_b\mu_b^o.$$

After mixing, we get

$$G_{after} = n_a[\mu_a^o + RT\ln\chi_a] + n_b[\mu_b^o + RT\ln\chi_b].$$

The free energy change on mixing is therefore

$$\begin{aligned}\Delta G_{mix} &= G_{after} - G_{before} \\ &= n_aRT\ln\chi_a + n_bRT\ln\chi_b.\end{aligned}$$

If $n = n_a + n_b$ then we can re-express ΔG_{mix} in terms of mole fractions

$$\boxed{\Delta G_{mix} = nRT[\chi_a\ln\chi_a + \chi_b\ln\chi_b].} \tag{20.33}$$

Again, since χ_a and χ_b are both less than 1, $\ln\chi_a$ and $\ln\chi_b$ are negative. The Gibbs free energy of mixing ideal liquids is therefore negative and hence the process occurs spontaneously.

In addition, since

$$\left(\frac{\partial\Delta G_{mix}}{\partial T}\right)_p = -\Delta S_{mix}$$

it follows that the entropy of mixing ideal liquids is

$$\boxed{\Delta S_{mix} = -nR[\chi_a \ln \chi_a + \chi_b \ln \chi_b]}. \tag{20.34}$$

You can see that $\Delta S_{mix} > 0$. The entropy increases with mixing.

Next, we get the enthalpy of mixing from

$$\begin{aligned}\Delta G_{mix} &= \Delta H_{mix} - T\Delta S_{mix} \\ \Delta H_{mix} &= \Delta G_{mix} - T\Delta S_{mix}\end{aligned}$$

thus

$$\boxed{\Delta H_{mix} = 0}, \tag{20.35}$$

showing that there is no enthalpy change on mixing liquids to form ideal solutions.

Finally, since

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

$$\boxed{\Delta V_{mix} = 0}. \tag{20.36}$$

This means that the volumes are additive.

Demo opportunity There is a demo that can be done here. Take a very large column of pure 200 proof ethanol. Add to it some water carefully. Initially you will see that the volumes look additive. Now invert the column and let the liquids mix. When brought back to its original state you will notice that the total volume has decreased and that the volumes are in fact not additive. This is non-ideal behavior. What is this telling you? A video of this can be found on the web.

Raoult's Law

The French chemist Francois Raoult found that the ratio of the partial vapor pressure of each component in a mixture (p_a) to its vapor pressure as a pure liquid (p_a^*) equals the mole fraction of the component

$$\boxed{\tfrac{p_a}{p_a^*} = \chi_a}. \tag{20.37}$$

Mixtures which obey Raoult's Law are called ideal solutions. They generally consist of two similar liquids. For example, toluene and benzene come to mind.

To illustrate, consider a solution composed of a volatile solvent and one or more involatile solutes. If the pure solvent (say A) is placed in an evacuated container (not all the way full though), the liquid will evaporate until the space above the liquid is filled with vapor. During the entire process the temperature is kept constant. At equilibrium, the pressure established in the vapor phase is p_a^* which is the vapor pressure of the pure liquid. Now if an involatile solute is dissolved in the liquid, and the entire experiment is repeated, the equilibrium pressure p_A over the solution (the solute is involatile so the vapor consists purely of solvent vapor, A) is observed to be less than p_a^*. This is then the basis of Raoult's observation. We generalize this to multiple volatile liquids.

Henry's Law

However, William Henry found experimentally that for real solutions at low (dilute) concentrations that although Raoult was basically correct for a solute, a, the constant of proportionality between p_a and χ_a is not really χ_a. Basically

$$p_a \neq p_a^* \chi_a.$$

Henry instead found that

$$p_a = \kappa_a p_a^* \tag{20.38}$$

where κ_a is a fudge factor.

Mixtures for which the solute obeys Henry's Law and the solvent obeys Raoult's Law are called ideal-dilute solutions.

Colligative properties

Finally, let's use what we learned about mixtures to describe what are called colligative properties. Here we will consider a substance (our solvent) into which we will introduce a **nonvolatile** solute. What we want to see is what happens to certain properties of the solvent. Namely, there are 3 colligative properties for solute/solvent mixtures that are typically discussed. We will cover the first two.

- Elevation of the boiling point
- Depression of the freezing point
- Osmotic pressure

Elevation of the boiling point

The equilibrium that we are interested in during the boiling process is between the solvent vapor and the solvent at 1 bar (basically 1 atm). Let's call the solvent A and the added solute B. A real world example would be adding salt to water to try and increase its boiling point. Does this actually work? Or is this just urban legend. Another example involves using ethylene glycol in your car's radiator to increase the boiling point of water. In fact, the boiling point increases 0.5 $^\circ C$ for every 76 grams added to 1 liter of water.

The equilibrium is established at a temperature where

$$\mu_A(g) = \mu_A(l)$$

since it's A that's doing the boiling. Next, we need expressions for the left hand side and the right hand side of the equation.

On the LHS we have

$$\mu_A(g) = \mu_A^\circ(g).$$

If you wanted to rationalize this, you would recall that the chemical potential expression for a gas is

$$\mu_A(g) = \mu_A^\circ(g) + RT\ln\frac{p}{p^\circ}$$

where its pressure p is just the same as p° (i.e. $p = p^\circ$).

On the RHS we know that

$$\mu_A(l) = \mu_A^\circ(l) + RT\ln\frac{p_A}{p_A^*}$$

where p_A is the partial pressure of the solvent in the presence of some solute. By Raoult's law we then have

$$\mu_A(l) = \mu_A^\circ(l) + RT\ln\chi_A.$$

Combining the left and right hand side expressions, we get

$$\mu_A^\circ(g) = \mu_A^\circ(l) + RT\ln\chi_A$$

and, in terms of the solute (i.e. $\chi_A = 1 - \chi_B$) we have

$$\begin{aligned}
\mu^\circ_A(g) &= \mu^\circ_A(l) + RT\ln(1-\chi_B) \\
\frac{[\mu^\circ_A(g) - \mu^\circ_A(l)]}{RT} &= \ln(1-\chi_B) \\
\frac{1}{R}\left[\frac{\mu^\circ_A(g)}{T} - \frac{\mu^\circ_A(l)}{T}\right] &= \ln(1-\chi_B).
\end{aligned}$$

At this point, take derivatives of both sides with respect to T under constant pressure conditions. We basically find terms like the following on the left hand side

$$\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right) = \frac{1}{T}\left(\frac{\partial \mu}{\partial T}\right)_p + \mu\left(-\frac{1}{T^2}\right)$$

where from $dG = Vdp - SdT$ we have $\left(\frac{\partial \mu}{\partial T}\right)_p = -S$. Thus,

$$\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right) = -\frac{S}{T} - \frac{\mu}{T^2}.$$

At this point, we replace $\mu = H - TS$ to get

$$\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right) = -\frac{H}{T^2}$$

and find that

$$\frac{1}{R}\frac{\partial}{\partial T}\left[\frac{\mu^\circ_A(g)}{T} - \frac{\mu^\circ_A(l)}{T}\right] = \frac{d}{dT}\ln(1-\chi_B)$$

becomes

$$\begin{aligned}
\frac{1}{R}\left[-\frac{H_A(g)}{T^2} + \frac{H_A(l)}{T^2}\right] &= \frac{d}{dT}\ln(1-\chi_B) \\
-\frac{1}{RT^2}[H_A(g) - H_A(l)] &= \frac{d}{dT}\ln(1-\chi_B) \\
-\frac{\Delta H_{vap}}{RT^2} &= \frac{d}{dT}\ln(1-\chi_B).
\end{aligned}$$

We can integrate the expression (assuming ΔH_{vap} to be independent of temperature) to get

$$\begin{aligned}
-\int_{T_b}^{T}\frac{\Delta H_{vap}}{RT'^2}dT' &= \int_{\chi_B=0}^{\chi_B} d\ln(1-\chi_B') \\
\left.\frac{\Delta H_{vap}}{RT'}\right|_{T_b}^{T} &= \ln(1-\chi_B) \\
\frac{\Delta H_{vap}}{R}\left(\frac{1}{T} - \frac{1}{T_b}\right) &= \ln(1-\chi_B).
\end{aligned}$$

If χ_B is small then $\ln(1-\chi_B) \simeq -\chi_B$. This gives

$$\chi_B = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_b} - \frac{1}{T}\right).$$

Finally, if $T \simeq T_b$

$$\chi_B \simeq \frac{\Delta H_{vap}}{R}\left(\frac{T - T_b}{TT_b}\right) = \frac{\Delta H_{vap}}{R}\frac{\Delta T}{T_b^2}.$$

Rearranging things gives our desired expression for the change in the solvent's boiling point with mole fraction of solute added

$$\boxed{\Delta T \simeq \left(\frac{RT_b^2}{\Delta H_{vap}}\right)\chi_B}. \tag{20.39}$$

The constant of proportionality in parenthesis is called the boiling point constant, k_b. Numerical values for k_b of some solvents can be found in the following table where recall that molality is moles of solute per kilogram of solvent.

Solvent	k_b (°C/molal)
benzene	2.53
phenol	3.04
water	0.51
ethanol	1.07
cyclohexane	2.79
acetic acid	3.08

Example

Say you had the idea that adding salt to water raises its boiling point. This would allow you to cook your pasta faster. How much salt would you need to add to raise the boiling point of water by 10 degrees? Let's assume that we are trying to boil 1L of water.

$$10 = (0.51)\left(\frac{\text{x mol NaCl}}{\text{1 kg water}}\right).$$

From this we find that $x = 19.61$ moles of NaCl. This is 1.15 kg or 2.53 lbs of salt. Even if you were to do this I doubt this would make your pasta palatable.

Old derivation of boiling point elevation formula

I'm leaving this older derivation of the boiling point elevation formula here for historical purposes. The derivation begins the same way by invoking

$$\mu_A(g) = \mu_A(l).$$

We then find expressions for the left and right hand sides of the equality. We find

$$\begin{aligned} \mu_A^o(g) &= \mu_A^o(l) + RT\ln a_A \\ \mu_A^o(g) &= \mu_A^o(l) + RT\ln \chi_A \end{aligned}$$

where $\chi_A + \chi_B = 1$ and where $p_A^* = p^o$ since the solute, B, is involatile. You can see this through the following gedanken experiment. Imaging that you have a flexible cover over the neat liquid (think of something like a balloon). The outside pressure is 1 bar. Under these conditions, the vapor in the balloon is exclusively the neat vapor of compound A. The associated vapor pressure is 1 bar since otherwise the outside air pressure would collapse the balloon. Likewise the balloon doesn't blow up either.

Now, rearrange the original expression above as

$$\mu_A^o(g) = \mu_A^o(l) + RT\ln(1-\chi_B)$$

or

$$\ln(1-\chi_B) = \frac{\mu_A^o(g) - \mu_A^o(l)}{RT} = \frac{\Delta G_{vap}}{RT}$$

where ΔG_{vap} is the molar Gibbs free energy of vaporization. At the same time

$$\Delta G_{vap} = \Delta H_{vap} - T_b\Delta S_{vap}.$$

If we invoke that $T \simeq T_b$ then we can replace ΔG_{vap} into our expression to find

$$\ln(1-\chi_B) \simeq \frac{\Delta H_{vap}}{RT} - \frac{\Delta S_{vap}}{R}.$$

Now when there is no B present (only A) then $\chi_B = 0$ and we get

$$\ln(1) = \frac{\Delta H_{vap}}{RT_b} - \frac{\Delta S_{vap}}{R} = 0$$

where T_b is the boiling point of A.

The difference then when some B is present is

$$\ln(1-\chi_B)-\ln(1)=\frac{\Delta H_{vap}}{RT}-\frac{\Delta H_{vap}}{RT_b}$$

which reduces to

$$\ln(1-\chi_B)=\frac{\Delta H_{vap}}{R}\left(\frac{1}{T}-\frac{1}{T_b}\right).$$

Now assume that χ_B (our solute) is small. $\chi_B \ll 1$. Then

$$\ln(1-\chi_B)\simeq -\chi_B$$

leaving

$$-\chi_B=\frac{\Delta H_{vap}}{R}\left(\frac{1}{T}-\frac{1}{T_b}\right)$$

or

$$\chi_B=\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_b}-\frac{1}{T}\right).$$

Finally, because we have already assumed that $T \simeq T_b$

$$\left(\frac{1}{T_b}-\frac{1}{T}\right)=\frac{T-T_b}{T_bT}\simeq\frac{T-T_b}{T_b^2}=\frac{\Delta T}{T_b^2}.$$

Thus

$$\chi_B\simeq\frac{\Delta H_{vap}\Delta T}{RT_b^2}$$

and we write

$$\Delta T=\left(\frac{RT_b^2}{\Delta H_{vap}}\right)\chi_B.$$

Depression of the freezing point

The heterogeneous equilibrium now of interest is between a pure solid solvent (A) and the solution with a solute (B) present within it at mole fraction χ_B. A real world example is adding salt to roads during the winter to prevent ice from forming. We can go about deriving the melting point depression formula in the same manner as we did for the boiling point elevation. I'll let you do that on your own. What follows is my original derivation.

At the freezing point, the chemical potentials of the two phases equal

$$\mu_A(s) = \mu_A(l)$$

where

$$\mu_A(l) = \mu_A^o(l) + RT\ln\chi_A$$

and we use $\mu_A(s) = \mu_A^o(s)$ on the left hand since the frozen solid is pure A (i.e. we implicitly assume that the solute B does not freeze out). The activity of a pure solid is $a = 1$ or $\chi_A = 1$ and thus the $RT\ln\chi$ term that would have been on the left hand side of the equation dies. Putting everything together gives

$$\mu_A^o(s) = \mu_A^o(l) + RT\ln\chi_A$$

where $\chi_A + \chi_B = 1$. We now do the same rearrangement/manipulation as before and instead of ΔH_{vap} we use ΔH_{fus}. We also assume that $T \simeq T_m$

$$\begin{aligned}
\mu_A^o(s) &= \mu_A^o(l) + RT\ln(1-\chi_B) \\
\frac{\mu_A^o(s) - \mu_A^o(l)}{RT} &= \ln(1-\chi_B) \\
\ln(1-\chi_B) &= \frac{\mu_A^o(s) - \mu_A^o(l)}{RT} = -\frac{\Delta G_{fus}}{RT} \\
\ln(1-\chi_B) &= -\frac{[\Delta H_{fus} - T_m\Delta S_{fus}]}{RT} \\
\ln(1-\chi_B) &= -\frac{\Delta H_{fus}}{RT} + \frac{\Delta S_{fus}}{R}.
\end{aligned}$$

If $\chi_B = 0$ (no solute, pure A) then

$$\ln(1) = -\frac{\Delta H_{fus}}{RT_m} + \frac{\Delta S_{fus}}{R} = 0$$

where T_m is the melting point of A.

The difference between $\ln(1-\chi_B) - \ln(1)$ is then

$$\begin{aligned}
\ln(1-\chi_B) &= -\frac{\Delta H_{fus}}{RT} + \frac{\Delta H_{fus}}{RT_m} \\
&= -\frac{\Delta H_{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)
\end{aligned}$$

where if χ_B is small, $\chi_B \ll 1$ and $\ln(1-\chi_B) \simeq -\chi_B$. Thus,

$$\begin{aligned}
-\chi_B &= -\frac{\Delta H_{fus}}{R}\left(\frac{1}{T}-\frac{1}{T_m}\right) \\
\chi_B &= \frac{\Delta H_{fus}}{R}\left(\frac{1}{T}-\frac{1}{T_m}\right) \\
\chi_B &= \frac{\Delta_{fus}}{R}\left(\frac{T_m - T}{TT_m}\right) \\
\chi_B &= \frac{\Delta H_{fus}(-\Delta T)}{RTT_m}.
\end{aligned}$$

Finally, recalling that we assumed $T \simeq T_m$

$$\chi_B = \frac{\Delta H_{fus}(-\Delta T)}{RT_m^2}$$

and

$$\boxed{\Delta T = -\tfrac{RT_m^2}{\Delta H_{fus}}\chi_B}. \tag{20.40}$$

This gives you the melting point depression when some solute B is put into a solvent A with an associated mole fraction χ_B. The constant of proportionality is called k_f, the freezing point constant. The table below lists k_f for some solvents.

Solvent	k_f ($^\circ C$/molal)
benzene	5.12
phenol	7.72
water	1.86
ethanol	2.00
cyclohexane	20.0

Example

How much salt does it take to lower the melting point of water by 5° C.? Assume we are dealing with 1 kg of water for convenience.

$$-5 = -1.86\left(\frac{\text{x moles NaCl}}{1\text{ kg}}\right)$$

so that $x = 2.25$ moles of NaCl. This is 120 grams.

Demo

A demo that can be done here is to make homemade ice cream using rock salt. You just need milk and sugar and some containers. Mix the milk and sugar in one small container. Mix the salt and water in a separate (larger) container. Then put the milk/sugar container into the salt water slurry and let it sit. Shake occasionally for best results. Better yet, have a student shake it for you during the entire lecture.

Chapter 21

Equilibrium

So far ΔG has been used to simply predict the spontaneity of a process or some reaction. But ΔG is more useful than this. It will be related to a reaction's equilibrium constant.

The reaction quotient, Q

To begin, we need some definitions. For a generalized reaction

$$\alpha A + \beta B \rightarrow \gamma C + \delta D$$

the reaction quotient Q is defined as

$$\boxed{Q = \frac{(a_C)^\gamma (a_D)^\delta}{(a_A)^\alpha (a_B)^\beta}} \tag{21.1}$$

where a_n is called the **activity** (seen in a previous chapter) and can be expressed as

- $a \propto \frac{[X]}{[X^o]}$ where $[X_o]$ is 1 M
- $a = \frac{p}{p^o}$ (ideal gas)
- $a = \frac{f}{p^o}$ (real gas where f is the fugacity)
- $a = \frac{p_i}{p_i^*}$ (liquids in a mixture, where p_i^* is the pure substance vapor pressure)

At equilibrium

$$Q = \frac{(a_C)^{\gamma}_{eq}(a_D)^{\delta}_{eq}}{(a_A)^{\alpha}_{eq}(a_B)^{\beta}_{eq}} = K_{eq}$$

or

$$\boxed{Q = K_{eq}}. \tag{21.2}$$

The equilibrium constant, K

Consider the reaction

$$aA + bB \rightleftharpoons cC + dD$$

The equilibrium constant is defined as

$$\boxed{K_c = \tfrac{[C]^c[D]^d}{[A]^a[B]^b}} \tag{21.3}$$

where the subscript c means that it is defined in terms of molar concentrations.

Alternatively, in discussing gas phase reactions, it is often convenient to write the equilibrium constant in terms of partial pressures. When you express the equilibrium constant for gaseous systems in terms of their partial pressures you call it K_p. In what follows, we will focus on so called "homogeneous" reactions for simplicity. "Heterogeneous" or mixed phase systems will be discussed later.

For example,

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

$$K_p = \frac{\left(\frac{p_{CH_4}}{p^o}\right)\left(\frac{p_{H_2O}}{p^o}\right)}{\left(\frac{p_{CO}}{p^o}\right)\left(\frac{P_{H_2}}{p^o}\right)}.$$

Now, in general, the value of K_p differs from that of K_c. To illustrate, let's consider the ideal gas case. For an ideal gas, the molar concentration of some species can be expressed as

$$[A] = \frac{n}{V} = \frac{p}{RT}.$$

Consider the generic reaction

$$\alpha A + \beta B \rightarrow \gamma C + \delta D$$

From this we get

$$\begin{aligned} K_c &= \frac{\left(\frac{p_c}{RT}\right)^{\gamma}\left(\frac{p_d}{RT}\right)^{\delta}}{\left(\frac{p_a}{RT}\right)^{\alpha}\left(\frac{p_b}{RT}\right)^{\beta}} \\ &= \frac{(RT)^{\alpha}(RT)^{\beta}}{(RT)^{\gamma}(RT)^{\delta}}\left(\frac{p_c^{\gamma}p_d^{\delta}}{p_a^{\alpha}p_b^{\beta}}\right) \\ &= RT^{\alpha+\beta-(\gamma+\delta)}\left(\frac{p_c^{\gamma}p_d^{\delta}}{p_a^{\alpha}p_b^{\beta}}\right). \end{aligned}$$

Thus

$$K_c = RT^{-\Delta n}K_p \tag{21.4}$$

or

$$\boxed{K_p = RT^{\Delta n}K_c}. \tag{21.5}$$

Remember here that Δn is the change in moles of gas molecules in the reaction. We take final minus initial.

The equilibrium constant for a sum of reactions

If a given chemical equation can be obtained by taking the sum of other sub reactions, the equilibrium constant for the given equation is the product of the equilibrium constants of these sub reactions.

Consider the following reactions

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

and

$$CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g).$$

If you sum these two reactions, together you get the overall reaction

$$CO(g) + 2H_2S \rightleftharpoons CS_2(g) + H_2O(g) + H_2(g).$$

The equilibrium constant for this reaction is therefore

$$K_{eq} = \frac{[CS_2][H_2O][H_2]}{[CO][H_2S]^2}.$$

I claim that this is the product of each individual reaction's equilibrium constant. Namely,

$$\begin{aligned} K_{1,eq} &= \frac{[CH_4][H_2O]}{[CO][H_2]^3} \\ K_{2,eq} &= \frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2}. \end{aligned}$$

Take the product of $K_{1,eq}$ and $K_{2,eq}$ and see what happens

$$\begin{aligned} K_{1,eq}K_{2,eq} &= \frac{[CH_4][H_2O]}{[CO][H_2]^3}\frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2} \\ &= \frac{[H_2O][CS_2][H_2]}{[CO][H_2S]^2} \\ &= K_{eq}. \end{aligned}$$

Good.

Other rules that K_{eq} follows

There are a bunch of rules for the equilibrium constant. I don't really want to go over them in any great detail because you should have already seen in this in general chemistry many years ago. I'm also a bit tired. So I'll just summarize things in bullet form.

The "rules"

- Pure solids and pure liquids are never ever included in the equilibrium constant expression. Don't do it. If you recall doing weak acid/base problems where you were asked to find the pH for a give concentration, remember you always set up your (R)ICE table and then ran the numbers. At the end, when relating the concentrations at equilibrium to K_a, you never ever included the concentration of the water solvent.

- The equilibrium constant depends on the way the reaction equation is written. So basically, you will get a different looking equilibrium constant if the reaction stoichiometries of the reaction are all changed.

For example, if you double all of the coefficients in your equation, K_{eq} will change. Or if you halve all the coefficients, K_{eq} will differ again. I'll let you play with this idea on your own.

- The equilibrium constant written for a reaction one way is just the reciprocal of K for the opposite way. So if you flip the orientation of the reaction, take the inverse of the old equilibrium constant to get the new equilibrium constant. Again, you can play with this idea on your own if interested.
- K_c and K_p do not equal. We've just seen how they are related. Note that when you get equilibrium constants from ΔG, as you will do in a minute, what you actually get are K_p values by convention. Some texts seem to omit this fact.
- For consecutive reactions, the overall equilibrium constant is simply the product of their individual equilibrium constants. We just saw this worked out above.

The relationship between free energy and the equilibrium constant

You've already seen a preview of this in one of our preceding examples. But we will do this again under a more generic scenario.

Consider the reaction

$$A + B \to C + D$$

The net change in chemical potential is

$$\Delta\mu = (\mu_C + \mu_D) - (\mu_A + \mu_B)$$

where in terms of activities we have (we basically have a mixture, right?)

$$\begin{aligned}
\mu_A &= \mu_A^o + RT\ln a_A \\
\mu_B &= \mu_B^o + RT\ln a_B \\
\mu_C &= \mu_C^o + RT\ln a_C \\
\mu_D &= \mu_D^o + RT\ln a_D.
\end{aligned}$$

Putting it all together then gives

$$\begin{aligned}\Delta\mu &= [\mu_C^o + RT\ln a_C + \mu_D^o + RT\ln a_D] - [\mu_A^o + RT\ln a_A + \mu_B^o + RT\ln a_B] \\ &= [(\mu_C^o + \mu_D^o) - (\mu_A^o + \mu_B^o)] + RT\ln a_C a_D - RT\ln a_A a_B \\ &= \Delta\mu^o + RT\ln\frac{a_C a_D}{a_A a_B} \\ &= \Delta\mu^o + RT\ln Q.\end{aligned}$$

At equilibrium, $\Delta\mu = 0$ and $Q = K_{eq}$

$$\begin{aligned}0 &= \Delta G^o - RT\ln K_{eq} \\ &= \Delta\mu^o - RT\ln K_{eq}\end{aligned}$$

or

$$\boxed{\Delta G^o = -RT\ln K_{eq}}. \tag{21.6}$$

I want to point out that the temperature listed above is tied to the ΔG value being used. So if you see ΔG^o, this means that the value of T you have to use is $T = 298$ K. You cannot just randomly put another temperature in there. If we have ΔG at another temperature, then you use that temperature for T. So basically

$$\begin{aligned}\Delta G^o(T_1) &= -RT_1\ln K_{eq}(T_1) \\ \Delta G^o(T_2) &= -RT_2\ln K_{eq}(T_2) \\ \Delta G^o(T_3) &= -RT_3\ln K_{eq}(T_3) \\ &\quad \text{etc}\ldots\end{aligned}$$

An alternate expression commonly seen is

$$\boxed{K_{eq} = e^{\frac{-\Delta G^o}{RT}}}. \tag{21.7}$$

An important side note here is that by convention we get K_p (not K_c) values from this expression.

Let's mix things up a little. What if we had the general reaction with more complicated stoichiometries

$$\alpha A + \beta B \rightarrow \gamma C + \delta D.$$

The difference in chemical potentials is then

$$\Delta\mu = (\mu_C + \mu_D) - (\mu_A + \mu_B)$$

where as the reaction proceeds

$$\begin{aligned}
\mu_C &= \gamma\mu_C^o + \gamma RT\ln a_C \\
\mu_D &= \delta\mu_D^o + \delta RT\ln a_D \\
\mu_A &= \alpha\mu_A^o + \alpha RT\ln a_A \\
\mu_B &= \beta\mu_B^o + \beta RT\ln a_B.
\end{aligned}$$

Therefore,

$$\begin{aligned}
\Delta\mu &= [\gamma\mu_C^o + \gamma RT\ln a_C + \delta\mu_D^o + \delta RT\ln a_D] - [\alpha\mu_A^o + \alpha RT\ln a_A + \beta\mu_B^o + \beta RT\ln a_B] \\
&= [\gamma\mu_C^o + RT\ln a_C^\gamma + \delta\mu_D^o + RT\ln a_D^\delta] - [\alpha\mu_A^o + RT\ln a_A^\alpha + \beta\mu_B^o + RT\ln a_B^\beta] \\
&= [\gamma\mu_C^o + \delta\mu_D^o + RT\ln a_C^\gamma a_D^\delta] - [\alpha\mu_A^o + \beta\mu_B^o + RT\ln a_A^\alpha a_B^\beta] \\
&= [(\gamma\mu_C^o + \delta\mu_D^o) - (\alpha\mu_A^o + \beta\mu_B^o)] + RT\ln a_C^\gamma a_D^\delta - RT\ln a_A^\alpha a_B^\beta \\
&= [(\gamma\mu_C^o + \delta\mu_D^o) - (\alpha\mu_A^o + \beta\mu_B^o)] + RT\ln\frac{a_C^\gamma a_D^\delta}{a_A^\alpha a_B^\beta}.
\end{aligned}$$

We get

$$\Delta\mu = \Delta\mu^o + RT\ln Q$$

with

$$Q = \frac{a_C^\gamma a_D^\delta}{a_A^\alpha a_B^\beta}.$$

At equilibrium, $\Delta\mu = 0$ and $Q = K_{eq}$ so that

$$\begin{aligned}
\Delta\mu^o &= -RT\ln K_{eq} \\
\Delta G^o &= -RT\ln K_{eq}
\end{aligned}$$

or that

$$K_{eq} = e^{\frac{-\Delta G^o}{RT}}.$$

Again, as an aside, note that K_{eq} here is actually K_p (not K_c).

The chemical potential and equilibrium

Next, let's show how the chemical potential and equilibrium are related for a reaction. Start with our previous expression for the Gibbs free energy change under constant T and p conditions

$$dG = \sum_i \mu_i dn_i$$

where changes in the number of moles (dn_i) are the result of a chemical reaction.

Then note that these changes in moles of a species are not independent because they are related by the stoichiometry of the reaction. We express this for a given species as

$$n_i = n_i^o + \nu_i \xi$$

where n_i^o is the number of initial moles of a species, ν_i is a coefficient reflecting the stoichiometry of the reaction and ξ is called the advancement coefficient and has units of moles. Note that ν_i is a negative number for reactants and is a positive number for products.

To be a little more specific about ξ, for some generic reaction

$$\alpha A + \beta B \rightarrow \gamma C + \delta D$$

the advancement coefficient is

$$\begin{aligned} n &= n^o + \nu_i \xi \\ dn &= \nu_i d\xi \end{aligned}$$

or $d\xi = \frac{dn}{\nu_i}$ where $\nu_a = -\alpha$, $\nu_B = -\beta$, $\nu_C = \gamma$, and $\nu_D = \delta$.

This gives:

$$\begin{aligned} d\xi &= -\frac{dn_A}{\alpha}(\text{for species A}) \\ &= -\frac{dn_B}{\beta}(\text{for species B}) \\ &= +\frac{dn_C}{\gamma}(\text{for species C}) \\ &= +\frac{dn_D}{\delta}(\text{for species D}) \end{aligned}$$

and in general

$$\boxed{d\xi = \tfrac{dn_i}{\nu_i}}. \tag{21.8}$$

From the above relationship, we get

$$dn_i = \nu_i d\xi.$$

Thus, since $dG = \mu_a dn_a + \mu_b dn_b + \mu_c dn_c + \ldots$

$$\begin{aligned} dG &= \sum_i \mu_i \nu_i d\xi \\ &= \left(\sum_i \mu_i \nu_i \right) d\xi. \end{aligned}$$

This can get rearranged to

$$\begin{aligned} \left(\frac{\partial G}{\partial \xi} \right)_{T,p} &= \left(\sum_i \mu_i \nu_i \right) \\ &= -\alpha\mu_a - \beta\mu_B + \gamma\mu_C + \delta\mu_D \\ &= [\gamma\mu_C + \delta\mu_D] - [\alpha\mu_A + \beta\mu_B]. \end{aligned}$$

The equation reflects the rate of increase of the Gibbs free energy with the advancement, ξ, of the reaction.

- if $\left(\frac{\partial G}{\partial \xi}\right)_{T,p} < 0$, the reaction goes right, towards products
- if $\left(\frac{\partial G}{\partial \xi}\right)_{T,p} > 0$, the reaction goes left, towards reactants
- if $\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = 0$, the reaction doesn't go anywhere, it's at equilibrium

Note that the last equilibrium expression can also be written as

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,p} = \sum_u \mu_i \nu_i = 0.$$

Thus you see that the derivative $\left(\frac{\partial G}{\partial \xi}\right)_{T,p}$ has the form of a change in Gibbs free energy since it is the sum of the chemical potentials of the products (positive ν_i) minus the sum of the chemical potentials of the reactants (negative ν_i).

Consequently, people often write $\Delta G = \left(\frac{\partial G}{\partial \xi}\right)_{T,p}$ and call it the reaction Gibbs free energy. Sometimes people will write ΔG_r or $\Delta_r G$ to make this clear.

$$\boxed{\Delta G = \sum_i \mu_i \nu_i} \tag{21.9}$$

So at equilibrium

$$\boxed{\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \Delta G = \Delta G_r = \Delta_r G = 0}. \tag{21.10}$$

All expressions are valid.

Now back to our equilibrium considerations Consider a model generic reaction

$$A \rightarrow B.$$

In addition, assume that A and B are gases. If we solely consider A then we get

$$G = G^o + n_A RT \ln \frac{p_A}{p^o}$$

where $p^o = 1$ bar and from where we also get

$$\left(\frac{\partial G}{\partial n_A}\right) = \left(\frac{\partial G^o}{\partial n_A}\right) + RT \ln \frac{p_A}{p^o}$$

or

$$\mu_A = \mu_A^o + RT \ln \frac{p_A}{p^o}.$$

We can do the same with B (assuming it's alone) to get

$$\mu_B = \mu_B^o + RT \ln \frac{p_B}{p^o}.$$

Now back to the reaction A little bit of A (dn_A) reacts to form a little bit of B (dn_B). Here $dn = |dn_A| = |dn_B|$. Then the free energy change of the system due to this little reaction under constant T and p conditions is

$$\begin{aligned}
dG &= -\mu_A dn + \mu_B dn \\
&= -(\mu_A^o + RT \ln \frac{p_A}{p^o})dn + (\mu_B^o + RT \ln \frac{p_B}{p^o})dn \\
&= dn(\mu_A^o - \mu_B^o + RT \ln \frac{p_B}{p^o} - RT \ln \frac{p_A}{p^o}) \\
\left(\frac{\partial G}{\partial n}\right)_{T,p} &= (\mu_A^o - \mu_b^o) + RT \ln \frac{p_B}{p_A} \\
&= \Delta G^o + RT \ln \frac{p_B}{p_A}
\end{aligned}$$

This term $\left(\frac{dG}{dn}\right)_{T,p}$ is referred to as the reaction Gibbs free energy and is essentially the slope of the Gibbs free energy plotted against the extent of a reaction. If $\left(\frac{dG}{dn}\right)_{T,p}$ is negative, the forward reaction will be spontaneous. If $\left(\frac{dG}{dn}\right)_{T,p}$ is positive the backward reaction to reactants will be spontaneous. At equilibrium, $\left(\frac{dG}{dn}\right) = 0$ or alternatively "$\Delta G = 0$" and

$$\begin{aligned} \Delta G^o &= -RT \ln \frac{p_B}{p_A} \\ &= -RT \ln K_{eq}. \end{aligned}$$

Alternatively,

$$K_{eq} = e^{\frac{-\Delta G^o}{RT}}$$

Finally, as mentioned before, K_{eq} here is K_p (not K_c) by convention.

These are the expressions you see all the time everywhere. Also apart from re-deriving these important expressions we come to another important conclusion.

$$\begin{aligned} dG &= -\mu_A dn + \mu_B dn \\ \left(\frac{dG}{dn}\right)_{T,p} &= -\mu_A + \mu_B = 0. \end{aligned}$$

Therefore,

$$\boxed{\mu_A = \mu_B} \tag{21.11}$$

at equilibrium. The chemical potential of A equals the chemical potential of B at equilibrium. "**A chemical reaction comes to equilibrium at constant T and p when the chemical potential of the reactants equals the chemical potential of the products.**"

More equilibrium stuff, definitions and such

Definition: A homogeneous equilibrium is an equilibrium that involves reactants and products in a single phase.
Definition: A heterogeneous equilibrium is an equilibrium involving reactants and products in more than one phase.

For example: Consider the reaction

$$3Fe(s) + 4H_2O(g) \rightleftharpoons F_3O_4(s) + 4H_2(g).$$

This reaction involves both solids and gases. The equilibrium constant is

$$K_c = \frac{[H_2]^4}{[H_2O]^4}.$$

Note that the equilibrium constant omits the solids and liquids because the volumes of solids and liquids are basically constant. Their activities are therefore 1. **The activities of solids and liquids equal 1**.

Examples

Write the equilibrium constant for the following reaction

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

or its reverse reaction

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

or this reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

all in terms of K_c and K_p.

Ans:

$$\begin{aligned} K_c &= \frac{[CH_4][H_2O]}{[CO][H_2]^3} \\ K_p &= \frac{p_{CH_4}p_{H_2O}}{p_{CO}p_{H_2}^3} \end{aligned}$$

$$\begin{aligned} K_c &= \frac{[CO][H_2]^3}{[CH_4][H_2O]} \\ K_p &= \frac{p_{CO}p_{H_2}^3}{p_{CH_4}p_{H_2O}} \end{aligned}$$

$$\begin{aligned} K_c &= \frac{[NH_3]^2}{[N_2][H_2]^3} \\ K_p &= \frac{p_{NH_3}^2}{p_{N_2}p_{H_2}^3} \end{aligned}$$

Example

Formulate an expression for the equilibrium constant, K_p, of the following reaction in terms of its degree of dissociation

$$Ni(CO)_4(g) \rightleftharpoons Ni(s) + 4CO(g).$$

Ans: The equilibrium constant of this heterogeneous equilibrium is

$$\begin{aligned} K_p &= \frac{\left(\frac{p_{CO}}{p^o}\right)^4}{\frac{p_{Ni(CO)_4}}{p^o}} \\ &= \frac{p_{CO}^4}{p_{Ni(CO)_4}} \end{aligned}$$

where we have divided out the units. All the pressures are just numbers.

The total number of moles of gas molecules is $1 + 3\alpha$. Therefore the partial pressures are

$$\begin{aligned} p_{CO} &= \frac{4\alpha}{1+3\alpha} p_{tot} \\ p_{Ni(CO)_4} &= \frac{1-\alpha}{1+3\alpha} p_{tot}. \end{aligned}$$

Plug everything into K_{eq} to get

$$K_p = \frac{(4\alpha)^4 p_{tot}^3}{(1-\alpha)(1+3\alpha)^3}$$

Example

Consider the reaction

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

at 298K. Show how K_{eq} is related to the partial pressures and free energy change of the species at equilibrium.

Ans: From freshman chemistry, you know how to answer this question immediately. However, let's do it a little differently to emphasize what we have been learning.

$$\begin{aligned} \mu_{NH_3} &= [2G^o_{NH_3} + 2RT \ln a_{NH_3}] \\ \mu_{N_2} &= [G^o_{N_2} + RT \ln a_{N_2}] \\ \mu_{H_2} &= [3G^o_{H_2} + 3RT \ln a_{H_2}] \end{aligned}$$

where

$$\begin{aligned} a_{NH_3} &= \frac{p_{NH_3}}{p^o} \\ a_{N_2} &= \frac{p_{N_2}}{p^o} \\ a_{H_2} &= \frac{p_{H_2}}{p^o}. \end{aligned}$$

Preview The change in free energy is

$$\begin{aligned} \Delta\mu &= [2\mu^o_{NH_3} - (\mu^o_{N_2} + 3\mu^o_{H_2})] + 2RT\ln a_{NH_3} - RT\ln a_{N_2} - 3RT\ln a_{H_2} \\ &= \Delta G^o + RT\ln\frac{a^2_{NH_3}}{a_{N_2}a^3_{H_2}} \end{aligned}$$

where $Q = \frac{a^2_{NH_3}}{a_{N_2}a^3_{H_2}}$. At equilibrium, $\Delta\mu = 0$ and $Q = K_{eq}$. Thus,

$$0 = \Delta G^o + RT\ln K_{eq}$$

and this gets rearranged to

$$K_{eq} = K_p = \frac{p^2_{NH_3}}{p_{N_2}p^3_{H_2}} = e^{\frac{-\Delta G^o}{RT}}$$

which is unitless, recall because each one of those partial pressures has already been divided by p^o.

The temperature dependence of the equilibrium constant

The temperature dependence of the equilibrium constant is found using the vant Hoff equation, which we saw earlier when first introducing the Gibbs free energy. In this section, we derived

$$K_p = e^{-\frac{\Delta G^o}{RT}}.$$

relating K_p with ΔG^o. However, this expression cannot be used to find K_p at different temperatures using ΔG^o expressed at 298 K. Namely, it might be tempting to use the above expression and insert into it a different temperature to get K_p at the new temperature. However, this only works if we know what ΔG^o is at the new temperature.

I won't derive the vant Hoff equation again. Rather, I'll just list it here and if you are interested you can go back to the free energy chapter to see it derived. The vant Hoff equation is

$$\ln \frac{K(T_2)}{K(T_1)} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

As an aside, you may have noticed in the past that the vant Hoff equation looks very similar to the Clausius-Clapeyron equation which we invoke when talking about phase diagrams. You have reason to notice the similarity because the vant Hoff and Clausius-Clapeyron equations are related.

Consider the following equilibrium

$$H_2O(l) \rightleftharpoons H_2O(g).$$

The associated equilibrium constant of this phase transition is $K_p = p(H_2O)$. We don't include the pure liquids or solids in the expression. Remember? Also we have ΔH_{vap} for the enthalpy of the transition. Then inserting this into the vant Hoff equation gives

$$\ln \frac{p(T_2)}{p(T_1)} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

which is the Clausius-Clapeyron equation.

Example

Consider the following reaction

$$PbCO_3(s) \rightleftharpoons PbO(s) + CO_2(g)$$

where $K_p = 2.7 \times 10^{-8}$ at 25^oC. $\Delta H^o = 88.3$ kJ/mol. Calculate K_p at 1000 K.

Ans: The vant Hoff equation is

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

Plugging numbers into the equation then gives

$$\ln \frac{K_2}{K_1} = -\frac{88,300}{8.314}\left(\frac{1}{1000} - \frac{1}{298}\right) = 25.019.$$

Solving for K_2 gives

$$K_2 = K_1 e^{25.019} = 1.98 \times 10^3.$$

So one sees that the equilibrium constant went from 10^{-8} to 10^3 by changing the temperature. One could have already predicted this trend qualitatively by recalling LeChatelier's principle.

Example

Calculate the equilibrium constant, K_p for the following reaction, first at 298 K, and then at 900 °C

$$CH_4(g) + \frac{1}{2}O_2(g) \rightleftharpoons CH_3OH(l). \tag{21.12}$$

Given:

Compound	ΔH_f^o (kJ/mol)	ΔG_f^o (kJ/mol)
CH_4 (g)	-74.87	-50.8
CH_3OH (l)	-277.0	-174.7

Ans: We first need to find out what ΔG_{rxn} and ΔH_{rxn} is at 298 K using the provided information in the table.

$$\begin{aligned}\Delta G_{rxn} &= \Delta G_f^o(CH_3OH, l) - \Delta G_f^o(CH_4, g)\\ &= -174.7 + 50.8\\ &= -123.9kJ\end{aligned}$$

$$\begin{aligned}\Delta H_{rxn} &= \Delta H_f^o(CH_3OH, l) - \Delta H_f^o(CH_4, g)\\ &= -277.0 + 74.9\\ &= -202.1kJ.\end{aligned}$$

Using this, we can find K_p at 298 K

$$\begin{aligned}K_p &= e^{-\frac{\Delta G_{rxn}}{RT}}\\ &= e^{\frac{123.9\times10^3}{(8.314)(298)}}\\ &= 5.22\times10^{21}.\end{aligned}$$

To get K_p at the 1173 K, we use the vant Hoff equation and assume that ΔH_{rxn} remains temperature independent.

$$\begin{aligned}\ln\frac{K_2}{K_1} &= -\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\\ &= \frac{202,100}{8.314}\left(\frac{1}{1173} - \frac{1}{298}\right)\\ &= -60.848.\end{aligned}$$

Then

$$K_2 = K_1 e^{-60.848} = 1.96\times10^{-5}.$$

Note that we could have qualitatively guessed this knowing LeChatelier's principle.

Example

Silver (I) oxide forms from silver and oxygen by the following reaction

$$4Ag(s) + O_2(g) \rightleftharpoons 2Ag_2O(s).$$

What is the pressure of O_2 in equilibrium with Ag_2O and Ag at 25^{o}C? At what temperature would the pressure of O_2 be equal to 1 atm.

Given:

Compound	ΔH_f^o (kJ/mol)	ΔG_f^o (kJ/mol)
Ag_2O (s)	-31.1	-11.32

Ans: First, evaluate what ΔG_{rxn} and ΔH_{rxn} are at 298 K.

$$\Delta G_{rxn} = 2\Delta G_f^o(Ag_2O, s) = -22.64kJ$$
$$\Delta H_{rxn} = 2\Delta H_f^o(Ag_2O, s) = -62.2kJ$$

Think about why we only included Ag_2O in the calculations. Why were $Ag(s)$ and $O_2(g)$ left out? Presumably you come to the conclusion that ΔG_f^o and ΔH_f^o for things in their standard states is defined to be zero.

Next, we calculate K_p

$$\begin{aligned} K_p &= e^{-\frac{\Delta G_{rxn}}{RT}} \\ &= e^{\frac{22.64\times 10^3}{(8.314)(298)}} \\ &= 9302. \end{aligned}$$

Finally, how is K_p linked to the pressure of oxygen? We know that pure liquids and solids are never included in the equilibrium constant. As a consequence,

$$K_p = \frac{1}{p_{O2}}.$$

Solving for p_{O2} then gives

$$p_{O2} = 1.07 \times 10^{-4}\text{bar}.$$

Part 2 of the problem wants us to get the temperature where $K_p = 1$. Using the vant Hoff equation

$$\begin{aligned} \ln\frac{K_2}{K_1} &= -\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ \ln\frac{1}{9302} &= -\frac{62.2(1000)}{8.314}\left(\frac{1}{T_2} - \frac{1}{298}\right) \end{aligned}$$

we solve for T_2 to get

$$T_2 = 468.5K.$$

Equilibrium, kinetic perspective

From a kinetics perspective (something we will see in a few chapters), the chemical equilibrium is the state reached by a reaction mixture when the rates of the forward and reverse reactions equal.

Consider the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g).$$

The rate of the forward reaction is

$$k_f[N_2O_4].$$

The rate of the reverse reaction is

$$k_r[NO_2]^2.$$

In the rate expressions, k_f and k_r are called rate constants. Again, we will see more of this later in the kinetics section.

At equilibrium, the forward and reverse rates equal

$$k_f[N_2O_4] = k_r[NO_2]^2.$$

The equilibrium constant is then the ratio of the forward and reverse rate constants. We can see this explicitly

$$K_c = \frac{k_f}{k_r} = \frac{[NO_2]^2_{eq}}{[N_2O_4]_{eq}}.$$

Similarly, consider another generic reaction

$$A + B \rightleftharpoons C$$

The rate of the forward reaction is

$$k_f[A][B].$$

The rate of the reverse reaction is

$$k_r[C].$$

At equilibrium, the forward and reverse rates equal

$$k_f[A][B] = k_r[C].$$

The equilibrium constant is then the ratio of the forward and reverse rate constants

$$K_c = \frac{k_f}{k_r} = \frac{[C]_{eq}}{[A]_{eq}[B]_{eq}}.$$

An analogous argument can be used in either example to relate K_p (partial pressures instead of concentrations) to the forward and reverse rate constants of a process.

Just like above, if the overall reaction occurs by a multistep mechanism, one can show that the equilibrium constant equals a product of the ratio of rate constants with one rate constant ratio for each step of the mechanism. Finally, write the equilibrium constant without units here to stay consistent with the above thermodynamic treatment using unitless activities.

Using the equilibrium constant

The equilibrium constant of a reaction can tell you a number of things.

- By looking at it, you can tell whether a particular equilibrium favors the products or reactants. Obviously the bigger the equilibrium constant is the more the products are favored. So if you see numbers that are much greater than 1, say 10^8, then we know that the products are favored. If you see numbers that are smaller than say 10^{-3} you know that the reactants are favored.

- When the equilibrium constant is about 1 (neither large nor small) neither reactants nor products are strongly favored.

- By looking at it and the reaction quotient, Q, you can tell the direction of a reaction.

- You can calculate the equilibrium concentration of a species of interest using it.

Example 1

Consider the synthesis of NH_3 from its elements

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g).$$

At 25 °C $K_c = 4.1 \times 10^8$ (obviously the products are favored). Suppose the equilibrium mixture is 0.01M N_2 and 0.01M H_2. Using K_c we can get the concentration of NH_3

$$K_c = \frac{[NH_3]^2}{(0.01)(0.01)^3} = 4.1 \times 10^8.$$

We find that

$$[NH_3] = 2.025M.$$

There is a whole lot more product than there are reactants at equilibrium, as predicted by the large K_c value. Conversely if the reaction had an equilibrium constant of 4.6×10^{-31} you would immediately say that at equilibrium there is a whole lot more reactants than products.

Example 2

Suppose a gaseous mixture from an industrial plant has the following composition at 1200 K.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

- 0.01M CO
- 0.02M H_2
- 0.001M CH_4
- 0.001M H_2O.

The equilibrium constant is $K_c = 3.92$ at that temperature (not particularly large). Which way does the reaction go?

Ans: We first determine the reaction quotient Q and relate it to K_c. The reaction quotient Q has the same form as the equilibrium constant but has concentration values that are not necessarily those at equilibrium. In this particular case,

$$\begin{aligned} Q &= \frac{[CH_4][H_2O]}{[CO][H_2]^3} \\ &= \frac{(0.001)(0.001)}{(0.01)(0.02)^3} \\ &= \frac{(0.001)^2}{0.08} \\ &= 12.5. \end{aligned}$$

Compare this with K_c. You see that $Q > K_c$ so the reaction will proceed left towards more reactants.

To summarize, for a generic reaction

$$\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$$

$$Q = \frac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta}$$

If

- $Q > K_{eq}$, the reaction goes left
- $Q < K_{eq}$, the reaction runs right
- $Q = K_{eq}$, the reaction doesn't move since its already at equilibrium

Example 2a, another reaction quotient problem

A 50 L reaction vessel contains 1 mol N_2, 3 mol H_2 and 0.5 mole NH_3. Will more NH_3 be formed or will it dissociate when the mixture goes to equilibrium at 400 °C. The equilibrium constant is $K_c = 0.5$ at this temperature.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Ans:

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3}.$$

The concentration of the various species are

$$[NH_3] = \frac{0.5mol}{50L} = 0.01M$$

$$[N_2] = \frac{1.0mol}{50L} = 0.02M$$

$$[H_2] = \frac{3.0mol}{50L} = 0.06M.$$

Put it all together

$$Q = \frac{(0.01)^2}{(0.02)(0.06)^3} = 23.15.$$

So $Q > K_c$ therefore the reaction runs left.

Example 2b, another reaction quotient problem

Carbon monoxide and hydrogen react in the presence of a catalyst to form methanol

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g).$$

An equilibrium mixture of these three substances is suddenly compressed so the final volume is half the initial value. In what direction does the reaction go as a new equilibrium is established?

Ans: Initially

$$K_{eq} = K_c = \frac{[CH_3OH]}{[CO][H_2]^2}.$$

After compression, the volume decreases by half, hence the old equilibrium concentration of each doubles.

$$\begin{aligned} Q &= \frac{2[CH_3OH]}{2[CO]4[H_2]^2} \\ &= \frac{1}{4}\frac{[CH_3OH]}{[CO][H_2]^2} \\ &= \frac{1}{4}K_{eq}. \end{aligned}$$

Since $Q < K_{eq}$ the reaction goes to the right, more products.

Example 3, determining equilibrium concentrations

In aqueous solution, iodide anions and molecular iodine reach an equilibrium in which triiodide is formed

$$I^-(aq) + I_2(aq) \rightleftharpoons I_3^-(aq).$$

The equilibrium constant is $K_c = 759$ at 25 °C. Calculate how much iodine remains in the solution as I_2 if 0.025 mol KI and 0.05 mol I_2 are dissolved together in 1 dm^3 of H_2O.

Ans: Starting values

- $I^- = 0.025M$
- $I_2 = 0.05M$

$$\begin{array}{rcl} I^- + I_2 & \rightleftharpoons & I_3^- \\ (0.025M - \alpha)(0.05 - \alpha) & & \alpha \end{array}$$

From the equilibrium constant, we get

$$\begin{aligned} K_c &= \frac{[I_3^-]}{[I^-][I_2]} \\ &= \frac{\alpha}{(0.025 - \alpha)(0.05 - \alpha)} = 759. \end{aligned}$$

This can be solved for α

$$\begin{aligned} \alpha &= 759(0.025 - \alpha)(0.05 - \alpha) \\ &= 759(0.00125 - 0.075\alpha + \alpha^2) \end{aligned}$$

to get

$$\alpha^2 - 0.0751 + 0.00125 = 0.$$

This is a quadratic equation, which we all know how to solve. We get

$$\alpha = 0.0376 \pm 0.0126.$$

For this to be physical, we must take the negative solution (think about it). Thus

$$\alpha = 0.025M$$

and the desired concentration is

$$\begin{aligned} [I_2] &= 0.05 - \alpha \\ &= 0.05 - 0.025 = 0.025M. \end{aligned}$$

Example 3a, determining equilibrium concentrations

Consider the gas phase reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

If 1 mol of N_2O_4 is introduced into a container and is allowed to reach equilibrium at a total gas pressure of p_{tot} bar, what are the equilibrium concentrations of each species.

Ans:

$$\begin{array}{ccc} N_2O_4(g) & \rightleftharpoons & 2NO_2(g) \\ (1-\alpha) & & 2\alpha \end{array}$$

The total moles of gas molecules is $(1-\alpha)+2\alpha = (1+\alpha)$. Thus the partial pressures of the different species are

$$\begin{aligned} P_{N_2O_4} &= \frac{(1-\alpha)}{(1+\alpha)} p_{tot} \\ P_{NO_2} &= \frac{2\alpha}{(1+\alpha)} p_{tot}. \end{aligned}$$

Divide each partial pressure by 1 bar to make the numbers unitless since we deal with activities.

$$\begin{aligned} K_p &= \frac{p_{NO_2}^2}{P_{N_2O_4}} \\ &= \frac{\left(\frac{2\alpha}{1+\alpha} p_{tot}\right)^2}{\left(\frac{1-\alpha}{1+\alpha} p_{tot}\right)} \\ &= \frac{4\alpha^2 p_{tot}}{(1-\alpha^2)}. \end{aligned}$$

We get

$$K_p = \frac{4\alpha^2 p_{tot}}{(1-\alpha^2)}.$$

Hence if you know K_p from thermodynamic data (ΔG data), the value of α can be found and the equilibrium concentrations of each species can be determined.

Additional examples

Example, applying stoichiometry to an equilibrium mixture

Carbon monoxide and hydrogen react according to the following equation

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O.$$

When 1 mole of CO and 3 mole of H_2 are placed in a 10 L vessel at 927 °C and are allowed to come to equilibrium, the mixture contains 0.387 mole

H_2O. What is the molar composition of the equilibrium mixture. That is, how many moles of each substance are present?

Ans:

$$\begin{array}{ccc} CO + 3H_2 & \rightleftharpoons & CH_4 + H_2O \\ (1-\alpha) \quad 3(1-\alpha) & & \alpha \quad \alpha \end{array}$$

But we know $\alpha = 0.387 mol$. Trivially then

- $[CO] = \frac{0.613 mol}{10L}$
- $[H_2] = \frac{1.839 mol}{10L}$
- $[CH_4] = \frac{0.387 mol}{10L}$
- $[H_2O] = \frac{0.387 mol}{10L}$

Example, degree of dissociation

Estimate the degree of dissociation at equilibrium for the following reaction

$$H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g).$$

The standard Gibbs energy of reaction for the decomposition is $\Delta G = 118$ kJ/mol at 2300K. Make reasonable simplifications or assumptions about α.

Ans:

$$\begin{array}{ccc} H_2O(g) & \rightarrow & H_2(g) + \frac{1}{2}O_2(g) \\ (1-\alpha) & & \alpha \quad \frac{\alpha}{2} \end{array}$$

The total number of moles of gas molecules is

$$n_{tot} = (1-\alpha) + (\alpha) + \frac{\alpha}{2} = 1 + \frac{\alpha}{2}.$$

The partial pressures are then

$$\begin{aligned} p_{O_2} &= \frac{\frac{\alpha}{2}}{(1+\frac{\alpha}{2})}p_{tot} \\ p_{H_2} &= \frac{\alpha}{(1+\frac{\alpha}{2})}p_{tot} \\ p_{H_2O} &= \frac{1-\alpha}{(1+\frac{\alpha}{2})}p_{tot} \end{aligned}$$

where $p_{tot} = 1$ bar. The equilibrium constant is

$$K_{eq} = \frac{p_{O_2}^{\frac{1}{2}} p_{H_2}}{p_{H_2O}}.$$

Note that we have divided all pressures by p^o so it is unitless

$$K_{eq} = \frac{\alpha^{\frac{3}{2}}}{\sqrt{2}\sqrt{1+\frac{\alpha}{2}}(1-\alpha)}.$$

We now make a simplification, namely that α is small so that

$$\begin{aligned} K_{eq} &\simeq \frac{\alpha^{\frac{3}{2}}}{\sqrt{2}\sqrt{1}(1)} \\ &\simeq \frac{\alpha^{\frac{3}{2}}}{\sqrt{2}} = e^{\frac{-\Delta G^o}{RT}}. \end{aligned}$$

When this is worked out

$$\begin{aligned} \alpha^{\frac{3}{2}} = \sqrt{2}(0.002) = 0.0029 \\ \alpha = 0.0205, \end{aligned}$$

meaning that approximately 2 percent of the water has decomposed.

Example, degree of dissociation

The standard Gibbs free energy of reaction for the decomposition of water

$$H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$$

is 135.2 kJ/mol at 2000K. Suppose steam at 200 kPa is passed through a tube furnace at that temperature. Calculate the mole fraction of O_2 present in the output gas stream.

Ans:

$$H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g) 1-\alpha \quad \alpha \quad \frac{1}{2}\alpha$$

$$K_{eq} = \frac{p_{O_2}^{\frac{1}{2}} p_{H_2}}{p_{H_2O}}$$

where again we have already divided each partial pressure by $p^o = 1$ bar to make this unitless and also where the total moles of gas molecules is $(1 + \frac{\alpha}{2})$

The partial pressures are

$$\begin{aligned} p_{O_2} &= \frac{\frac{\alpha}{2} p_{tot}}{(1 + \frac{\alpha}{2})} \\ p_{H_2} &= \frac{\alpha p_{tot}}{(1 + \frac{\alpha}{2})} \\ p_{H_2O} &= \frac{(1-\alpha) p_{tot}}{(1 + \frac{\alpha}{2})}. \end{aligned}$$

Putting it together gives

$$K_{eq} = \frac{\alpha^{\frac{3}{2}} \sqrt{p_{tot}}}{\sqrt{2}\sqrt{1 + \frac{\alpha}{2}}(1 - \alpha)}.$$

Now, assume that α is small, smaller than 1.

$$K_{eq} \simeq \frac{\alpha^{\frac{3}{2}} \sqrt{p_{tot}}}{\sqrt{2}\sqrt{1}(1)}$$

where $p_{tot} = 2$ bar. This yields

$$K_{eq} = \alpha^{\frac{3}{2}} = e^{\frac{-\Delta G^o}{RT}} = e^{\frac{-135200}{RT}}$$

thus

$$\begin{aligned} \alpha^{\frac{3}{2}} &= 0.00029 \\ \alpha &= 0.0044. \end{aligned}$$

But we're not completely done yet. We need $\frac{1}{2}\alpha$ for O_2 so

$$\frac{1}{2}\alpha = 0.00221.$$

This is the desired mole fraction of O_2. Note that if you run the problem the same way using the Vant Hoff equation you will find the same answer.

Catalysts and the equilibrium position

Catalysts do not change the position of equilibrium. This can be shown mathematically below.

Let ϵ_{cat} be the reduction in activation energy due to the catalyst. Now let the forward and backward activation energies with no catalyst be ϵ_a^f and ϵ_a^r respectively. What follows is basically a preview of the kinetics section of the class since we will take a kinetics perspective to equilibrium and of the equilibrium constant.

The Arrhenius equation (shown later, but assume it for now) for the forward and reverse rate constants in the presence of the catalyst is

$$\begin{aligned} k_f &= Ae^{\frac{-(\epsilon_a^f - \epsilon_{cat})}{RT}} \\ k_r &= Ae^{\frac{-(\epsilon_a^r - \epsilon_{cat})}{RT}}. \end{aligned}$$

The equilibrium constant is the ratio of the forward to reverse rate constants

$$\begin{aligned} K &= \frac{k_f}{k_r} = \frac{Ae^{\frac{-\epsilon_a^f}{RT}} e^{\frac{\epsilon_{cat}}{RT}}}{Ae^{\frac{-\epsilon_a^r}{RT}} e^{\frac{\epsilon_{cat}}{RT}}} \\ &= \frac{e^{\frac{-\epsilon_a^f}{RT}}}{e^{\frac{-\epsilon_a^f}{RT}}} \\ &= \frac{k_f(\text{no catalyst})}{k_r(\text{no catalyst})}. \end{aligned}$$

Thus, we see that K does not change with the presence of the catalyst. The equilibrium position is maintained. The only difference is that the catalyst has made it easier to achieve the equilibrium point by lowering all barriers to reaching it.

Le'Chatelier's Principle

I'm getting tired. So I'm sure that you can motivate Le'Chatelier's principle for yourself. Let's just walk through the various scenarios.

Le'Chatelier, changing the volume

If we are dealing with gases, decreasing the volume has the effect of increasing the pressure of the system. In the ideal gas scenario, we've already seen that Boyle's Law describes an inverse relationship between a gas' volume and pressure. Note that we are implicitly saying that the pressure of both the reactants and products will change. What we then find, if we look at an equilibrium constant, is that increasing the pressure will favor moving the reaction towards the direction that produces fewer molecules. So for example, if we have the generic gas phase reaction

$$A(g) + B(g) \rightleftharpoons C(g),$$

decreasing the volume of the container will increase the pressures of species A, B, and C and the reaction will favor moving towards the products in response to this change. Conversely, increasing the volume of the container will decrease all of the pressures and the resulting equilibrium constant will suggest that the reaction will move towards the reactants.

Similarly, increasing the volume has the same effect as decreasing the pressure of the system. The reaction moves in the direction which produces more molecules. In all cases, the equilibrium constant *does not* change.

Example

Consider an increase in the pressure of the generic reaction (this means we are magically, decreasing the volume of the container)

$$A \rightleftharpoons 2B$$

where

$$K_{eq} = \frac{p_B^2}{p_A}.$$

In response, le'Chatelier's principle simply says that the reaction will go towards more reactants in order to reduce the overall number of gas molecules.

We can show this quantitatively. Starting with

$$\begin{array}{rcl} A(g) & \rightleftharpoons & 2B(g) \\ 1-\alpha & \rightleftharpoons & 2\alpha \end{array}$$

the total number of moles in the reaction is

$$n_{tot} = (1-\alpha) + 2\alpha = (1+\alpha).$$

At equilibrium, the mole fractions of A and B are

$$\begin{aligned} \chi_A &= \frac{1-\alpha}{1+\alpha} \\ \chi_B &= \frac{2\alpha}{1+\alpha} \end{aligned}$$

and the partial pressures of each species are

$$\begin{aligned} p_A &= \left(\frac{1-\alpha}{1+\alpha}\right) p_{tot} \\ p_B &= \left(\frac{2\alpha}{1+\alpha}\right) p_{tot} \end{aligned}$$

where $p_{tot} = p_A + p_B$. The equilibrium constant is then

$$\begin{aligned} K_{eq} &= \frac{p_B^2}{p_A} \\ &= \frac{\frac{4\alpha^2}{(1+\alpha)^2} p_{tot}^2}{\left(\frac{1-\alpha}{1+\alpha}\right) p_{tot}} \\ &= \frac{4\alpha^2}{(1+\alpha)(1-\alpha)} p_{tot} \\ &= \left(\frac{4\alpha^2}{1-\alpha^2}\right) p_{tot} \end{aligned}$$

or

$$K_{eq} = \frac{4\alpha^2}{1-\alpha^2} p_{tot}.$$

Now solve for α

$$\begin{aligned} (1-\alpha^2) K_{eq} &= 4\alpha^2 p_{tot} \\ K_{eq} - \alpha^2 K_{eq} &= 4\alpha^2 p_{tot} \\ K_{eq} - \alpha^2 K_{eq} &= 4\alpha^2 p_{tot} \\ K_{eq} &= \alpha^2 K_{eq} + 4\alpha^2 p_{tot} \\ K_{eq} &= \alpha^2 (K_{eq} + 4 p_{tot}) \end{aligned}$$

to get

$$\begin{aligned} \alpha^2 &= \frac{K_{eq}}{K_{eq} + 5 p_{tot}} \\ &= \frac{1}{1 + \frac{4 p_{tot}}{K_{eq}}}. \end{aligned}$$

We choose the positive solution since the negative solution of the square root is unphysical. Note that K_{eq} is a constant here

$$\alpha = \frac{1}{\sqrt{1 + \frac{4 p_{tot}}{K_{eq}}}}.$$

You can see here that if $p_{tot} = p_A + p_B$ increases then α just decreases and more of the reactants are left. The reaction effectively shifts to the left.

Another example

Consider the reaction

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g).$$

The overall number of gas moles decreases with the reaction moving towards products. Le'Chatelier's principle therefore says that an increase in the pressure due to both reactants and products will push the reaction to the right. Let's see this quantitatively. Starting with

- partial pressure $NH_3 = \chi_{NH_3} p_{tot}$
- partial pressure $N_2 = \chi_{N_2} p_{tot}$
- partial pressure $H_2 = \chi_{H_2} p_{tot}$,

the equilibrium constant can be written as

$$\begin{aligned} K_{eq} &= \frac{p^2_{NH_3}}{p_{N_2} p^3_{H_2}} \\ &= \frac{\chi^2_{NH_3} p^2_{tot}}{\chi_{N_2} p_{tot} \chi^3_{H_2} p^3_{tot}} \\ &= \frac{\chi^2_{NH_3}}{\chi_{N_2} \chi^3_{H_2}} \left(\frac{1}{p^2_{tot}} \right). \end{aligned}$$

Let $k_x = \left(\frac{\chi^2_{NH_3}}{\chi_{N_2} \chi^2_{H_2}} \right)$, then

$$K_{eq} = \frac{k_x}{p^2_{tot}}.$$

So you can see that if $p_{tot} = p_{N2} + p_{H2} + p_{NH3}$ increases two times, then k_x must increase four times to allow K_{eq} to remain the same. Next, if k_x increases four times then χ_{NH_3} must increase meaning that the reaction shifts to the right.

Le'Chatelier, changing the temperature

The effect of changing the system's temperature depends on whether the reaction involved is exothermic or endothermic. If it is exothermic, le Chatelier says that heating the system will shift the reaction in the direction which absorbs energy (i.e. the endothermic direction). If the reaction is endothermic, heating the system will move the reaction towards more products products.

This can be shown mathematically.

$$\Delta G^o = -RT\ln K_{eq}$$

thus

$$\ln K_{eq} = -\frac{\Delta G^o}{RT}$$

where $\Delta G^o = \Delta H^o - T\Delta S^o$ and

$$\ln K_{eq} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}.$$

Now, if you make the assumption that ΔH^o and ΔS^o are independent of T over the range studied

$$\boxed{\frac{d\ln K_{eq}}{dT} = \frac{\Delta H^o}{RT^2}.} \tag{21.13}$$

Recall that this is called the Vant Hoff equation. But it's really the same as the Gibbs-Helmholtz equation seen earlier.

You can seen that for an exothermic reaction ΔH^o is negative. K_{eq} will therefore decrease giving you more reactants. Conversely, if the reaction is endothermic, ΔH^o is positive and K_{eq} will increase giving more products. Let's integrate the Vant Hoff equation to see what happens

$$\begin{aligned} \ln K_{eq}|_{K_{eq1}}^{K_{eq2}} &= -\frac{\Delta H^o}{RT}|_{T_1}^{T_2} \\ \ln K_{eq2} - \ln K_{eq1} &= \frac{-\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right). \end{aligned}$$

Therefore

$$\boxed{\ln K_{eq2} = \ln K_{eq1} + \frac{-\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}. \tag{21.14}$$

This describes how the equilibrium constant will change with temperature. Alternatively, sometimes people write

$$\boxed{\ln\frac{K_{eq2}}{K_{eq1}} = \frac{-\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}. \tag{21.15}$$

Le'Chatelier, adding and removing reactants or products

This will shift the reaction left or right, depending on what you add or what you remove. For example, adding products to a system at equilibrium will shift the reaction towards reactants. Likewise, removing reactants will shift the reaction to the reactants side. Adding reactants will shift the reaction towards products. Likewise, removing products will shift the reaction this way. One can quantitatively see this by looking at the equilibrium constant and playing with the values in the numerator or denominator.

Le'Chatelier, changing the pressure with an inert gas

One can change the pressure of a reaction using an inert gas. The case of adding a reactive gas is the same as adding more reactant or more product to the mix so we don't consider it here. In the inert gas case, increasing or decreasing the overall pressure with it *will not* change the equilibrium constant since this term is not present in either the numerator or denominator of K_{eq}. So nothing happens.

Example

A and B react to produce C according to the following generic chemical reaction

$$A + B \rightarrow C.$$

Additional amounts of A and B are added to an equilibrium mixture of A, B, and C such that when equilibrium is again attained, the amounts of A and B are doubled in the same volume. How is the amount of C changed?

Ans: Originally

$$K_{eq} = \frac{[C]}{[A][B]}.$$

At the new equilibrium point, you have $2[A]$ and $2[B]$. Since K_{eq} does not change, for the ratio to stay the same, we must have $[C]_{new} = 4[C]$.

Le'Chatelier, catalyst

Adding a catalyst has no effect on the equilibrium position. You just get there faster.

Chapter 22

Recap

I want to recap everything before moving into the kinetics part of this class.

At this point, we should be able to take data from the literature in terms of ΔH_f^o as well as heat capacities and calculate ΔH and ΔS at any temperature as well as calculate ΔG and K_{eq} (actually K_p).

We will run though 2 such examples where you will "put it all together".

Example 1

Silver carbonate decomposes on heating. Calculate the equilibrium constant at 110^o C for the reaction

$$Ag_2CO_3(s) \rightarrow Ag_2O(s) + CO_2(g)$$

given (units of kJ/mol)

$$\begin{aligned} \Delta H_f^o(Ag_2CO_3(s)) &= -501.4 \\ \Delta H_f^o(Ag_2O(s)) &= -29.07 \\ \Delta H_f^o(CO_2(g)) &= -393.5 \end{aligned}$$

and (units of J/mol K)

$$\begin{aligned} \Delta S^o(Ag_2CO_3(s)) &= 167.3 \\ \Delta S^o(Ag_2O(s)) &= 121.7 \\ \Delta S^o(CO_2(g)) &= 213.7 \end{aligned}$$

and (units of J/mol K)

$$\begin{aligned} C_p(Ag_2CO_3(s)) &= 109.6 \\ C_p(Ag_2O(s)) &= 68.6 \\ C_p(CO_2(g)) &= 37.1. \end{aligned}$$

Ans: We have to get ΔS and ΔH at 383K (110^o C).

$$\begin{aligned} \Delta S_{383} &= \Delta S^o_{298} + \bar{C}_p ln \frac{T_2}{T_1} \\ \Delta H_{383} &= \Delta H^o_{298} + \bar{C}_p (T_2 - T_1). \end{aligned}$$

But first we want ΔS_{298} and ΔH_{298} to allow the above Kirchoff type evaluation. Plugging in the numbers from our table we get

$$\Delta S^o_{298} = (213.7) + (121.7) - (167.3) = 168.1 J/K$$

and

$$\Delta H^o_{298} = (-393.5) - (29.07) + (501.4) = 78.83 kJ.$$

Next,

$$\Delta S_{383} = 168.1 + \bar{C}_p \ln \frac{383}{298}$$

where

$$\bar{C}_p = 37.1 + 68.6 - 109.6 = -3.9 J/K.$$

We therefore have

$$\Delta S_{383} = 167.12 J/K.$$

At this point, we go after the enthalpy to get

$$\Delta H_{383} = 78.83 - \frac{3.9}{1000}(383 - 298)$$

giving

$$\Delta H_{383} = 78.5 kJ.$$

Now, we need to calculate the free energy change at 383K

$$\begin{aligned} \Delta G_{383} &= \Delta H_{383} - T \Delta S_{383} \\ &= 78.5 - (383.15)(0.167) \end{aligned}$$

yielding

$$\Delta G_{383} = 14.67 kJ.$$

The equilibrium constant at 383 K is therefore

$$K_p = e^{\frac{-\Delta G_{383}}{RT}}.$$

Plugging in the numbers, we get

$$K_{p,383} = 0.01.$$

Note that if you evaluate this using the Vant Hoff approach, you will (or should) obtain the same answer. Presumably you can do this on your own in your leisure time.

Example 2

The standard enthalpy of formation of H_2O is $\Delta H^o_{298} = -241.8$ kJ/mol. Use the mean heat capacities and standard entropies listed to estimate the percent dissociation of water vapor at 2000 °C and 0.01 bar.

The reaction of interest is

$$H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g).$$

We have

$$\Delta H^o_{298} = 241.8 kJ$$

where the entropies are (units of J/mol K)

$$\begin{aligned} \Delta S^o_{298}(H_2O(g)) &= 188.3 \\ \Delta S^o_{298}(H_2(g)) &= 130.7 \\ \Delta S^o_{298}(O_2) &= 205.1 \end{aligned}$$

along with the following heat capacities (units of J/mol K)

$$\begin{aligned} C_p(H_2O(g)) &= 33.6 \\ C_p(H_2(g)) &= 28.8 \\ C_p(O_2(g)) &= 29.4. \end{aligned}$$

From this, we get the net entropy change

$$\begin{aligned}\Delta S^o_{298} &= (\frac{1}{2}(205.1) + 130.7) - 188.3 \\ &= 44.95 J/K.\end{aligned}$$

Likewise, we can find the standard free energy change

$$\begin{aligned}\Delta G_{298} &= \Delta H_{298} - T_{298}\Delta S_{298} \\ &= 241.8 - \frac{298}{1000}(44.95) \\ &= 241.8 - 13.38 \\ &= 228.4 kJ.\end{aligned}$$

From the table, the net heat capacity of the reaction is

$$\begin{aligned}\bar{C_p} &= \frac{1}{2}(29.4) + 28.8 - 33.6 \\ &= 9.9 J/K.\end{aligned}$$

Now, let's get the enthalpy and entropy at 2273K using a Kirchoff type approach. First, the enthalpy

$$\begin{aligned}\Delta H^o_{2273} &= \Delta H^o_{298} + \bar{C_p}(T_2 - T_1) \\ &= \Delta H^o_{298} + 9.9(2273 - 298) \\ &= 241.8 + 19.6 \\ &= 261.35 kJ.\end{aligned}$$

Next, the entropy

$$\begin{aligned}\Delta S^o_{2273} &= \Delta S^o_{298} + \bar{C_p}\ln\frac{T_2}{T_1} \\ &= 44.95 + 9.9\ln\frac{2273}{298} \\ &= 65.06 J/K.\end{aligned}$$

Finally, the free energy change at 2273K.

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ \Delta G_{2273} &= 261.35 - 2273(0.065) \\ &= 113.46 kJ.\end{aligned}$$

At this point, use ΔG_{2273} to get the equilibrium constant at 2273 K

$$\begin{aligned} K_p &= e^{\frac{-\Delta G_{2273}}{RT}} \\ &= e^{-6.0}. \end{aligned}$$

Thus,

$$K_p = 0.0025.$$

One can calculate this number using the Vant Hoff approach. You will (or should) get an identical number.

We're not done yet. Gotta find the partial pressures at equilibrium

$$\begin{aligned} p_{O_2} &= \frac{\frac{1}{2}\alpha}{(1+\frac{1}{2}\alpha)} p_{tot} \\ p_{H_2} &= \frac{\alpha p_{tot}}{(1+\frac{1}{2}\alpha)} \\ p_{H_2O} &= \frac{1-\alpha}{1+\frac{1}{2}\alpha} p_{tot}. \end{aligned}$$

Plug this into K_p

$$\begin{aligned} K_p &= \frac{\frac{p_{O_2}}{p^o} p_{H_2}}{p_{H_2O}} \\ &= \frac{[\frac{\frac{1}{2}\alpha}{(1+\frac{1}{2}\alpha)} p_{tot}]^{\frac{1}{2}} [\frac{\alpha p_{tot}}{(1+\frac{1}{2}\alpha)}]}{[\frac{1-\alpha}{1+\frac{1}{2}\alpha} p_{tot}]} \\ &= \frac{\sqrt{0.5}\alpha^{\frac{3}{2}} p_{tot}^{\frac{1}{2}}}{(1-\alpha)(1+\frac{1}{2}\alpha)^{\frac{1}{2}}} = 0.0025. \end{aligned}$$

To simplify this expression, assume that α is small compared to 1 so the denominators drop out.

$$K_p \simeq \sqrt{0.5}\alpha^{\frac{3}{2}}(0.01)^{\frac{1}{2}} = 0.0025$$

or

$$\begin{aligned} \alpha^{\frac{3}{2}} &= 0.0353 \\ \alpha &= 0.1076. \end{aligned}$$

Done.

Chapter 23

Kinetics

Definition: The rate of a reaction is the amount of product formed or the amount of reactant used up per unit of time (an increase in molar concentration of the product per unit time) or (a decrease in the molar concentration of a reactant per unit time). The units are in $mol/l \cdot s$.

Dependence of the rate on concentration

Empirically it has been found that a reaction rate depends on the concentrations of reactants. So for example, considering the reaction

$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$$

the reaction rate doubles when the NO_2 concentration doubles. Alternatively, doubling the concentration of F_2 doubles the rate. We **empirically** find that the experimental rate is described by the equation

$$Rate = R = k[NO_2][F_2]$$

where k (the rate constant) is a proportionality constant and is constant at a fixed temperature. However, it varies with temperature as we will see, causing the rate to change. We will return to this later. Finally, the units of k will depend on the actual rate law (the above equation with the concentrations of reactants).

In general for a reaction

$$aA + bB \rightarrow cC + dD$$

we have the following

$$\boxed{R = k[A]^m[B]^n} \tag{23.1}$$

where m and n are frequently integers but not necessarily so. m and n must be determined *experimentally* and cannot be obtained by simply looking at the balanced equation. The overall order of the reaction is the sum of all the exponents (i.e. m+n).

Recall for the previous reaction we had

$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g).$$

The associated rate law was

$$R = k[NO_2]^1[F_2]^1.$$

Thus, you see that $m = 1$ and $n = 1$ has no relation with the reaction's actual stoichiometry. This is a second order (m+n=2) process.

Reaction order

Definition: The reaction order at constant temperature with respect to a given species is the exponent of the species in the rate law. So for example

$$R = k[NO_2][F_2]$$

is 1st order in NO_2 and 1st order in F_2. The overall order of the reaction is 2 since this is the sum of the exponents.

Examples of reaction order

A. The conversion of cyclopropane to propylene

$$C_3H_6(g) \rightarrow CH_2 = CHCH_3(g).$$

The rate law is found to be

$$R = k[C_3H_6].$$

The reaction is 1st order in C_3H_6 and 1st order overall.
B. The reaction of nitric oxide with hydrogen.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g).$$

Experimentally, one finds that the rate law is

$$R = k[NO]^2[H_2]$$

which is 2nd order in NO and 1st order in H_2, so the reaction is 3rd order overall.

Although these reaction orders happen to have whole numbers, they can be fractional numbers, negative (i.e. the reaction rate slows down when a reactant is present), or even zero (i.e. the reaction rate is independent of the reactant).

The rate of a reaction

By convention, the rate of a reaction, R, is defined in terms of the rate of change of the concentration of a reactant or a product.

$$\boxed{R = \frac{1}{\nu_i}\frac{d[X_i]}{dt} = \frac{1}{\nu_i V}\frac{d\xi}{dt}} \tag{23.2}$$

where

- ν_i reflects the stoichiometry of the species in a reaction
- $[X_i]$ is the concentration of the species of interest
- V is a volume
- ξ is called the extent of reaction and has unit of moles

So for example, the rate of

$$A + 2B \rightleftharpoons X$$

can be described by

$$R = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{d[X]}{dt}.$$

This definition has the advantage that the same rate of reaction R is obtained no matter which reactant or product is studied. **However, the rate of reaction does depend on how the stoichiometric equation is written. In discussing kinetics, equations with fractional stoichiometries are *avoided* even though this is completely legitimate in thermodynamics**.

To summarize

- If the reaction goes forward, R is positive
- If the reaction goes backwards, R is negative

- If the reaction is at equilibrium, R equals zero

We will generally be concerned with reactions occurring at constant volume (not to be confused with the thermodynamics version.) We are still conducting the reaction at constant pressure. All we mean here is that the volume of the reaction vessel does not change.

Example, rate of reaction

The reaction

$$H_2 + Br_2 \rightarrow 2HBr$$

is carried out in a 0.25L reaction vessel. The change in the amount of Br_2 in 0.01s is -0.001 mol.

- (a) What is the rate of conversion $\frac{d\xi}{dt}$
- (b) What is the rate of reaction, R
- (c) What are the values of $\frac{d[H_2]}{dt}$, $\frac{d[Br_2]}{dt}$, and $\frac{d[HBr]}{dt}$

Ans:
(a) $\frac{d\xi}{dt} = \frac{0.001}{0.01} = 0.1 mol/s$
(b) $R = \frac{1}{V}\frac{d\xi}{dt} = \frac{1}{0.25L}(0.1 mol/s) = 0.4M/s$
(c)

$$\begin{aligned}\frac{d[H_2]}{dt} &= \frac{-1}{V}\frac{d\xi}{dt} = -0.4M/s \\ \frac{d[Br_2]}{dt} &= \frac{-1}{V}\frac{d\xi}{dt} = -0.4M/s \\ \frac{d[HBr]}{dt} &= \frac{2}{V}\frac{d\xi}{dt} = +0.8M/s.\end{aligned}$$

Example, dependence of reaction rate on the chemical reaction

Show that different rates are obtained when the same reaction is written different ways

$$\begin{aligned}2A + B &\rightarrow 2C \\ A + \frac{1}{2}B &\rightarrow C\end{aligned}$$

Ans: According to the first stoichiometric reaction we get

$$R = -\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt}.$$

According to the second stoichiometric reaction we get

$$R = -\frac{d[A]}{dt} = -2\frac{d[B]}{dt} = \frac{d[C]}{dt}.$$

This problem of varying reaction rate definitions is avoided by not using fractional numbers for the stoichiometry.

Time-dependent concentrations

Rate laws are differential equations. You have to integrate them if you want to find the concentration of a species as a function of time. They are frequently complicated though. As a consequence, if one cannot solve them analytically (paper and pencil), one must do it numerically. Here are some simple cases for reactions that are zeroth order overall, first order overall, and second order overall. These we can treat analytically. We will also consider some special higher order reactions.

Zeroth order overall

A reaction is zeroth order if the reaction rate is independent of the concentration of the reactants.

Consider the generic reaction

$$A \rightarrow B$$

where the reaction rate is

$$-\frac{d[A]}{dt} = k.$$

This expression can be integrated to find the time-dependent concentration of A.

$$\frac{d[A]}{dt} = -k$$

$$[A_2] - [A_1] = -k(t_2 - t_1)$$

Now if $t_1 = 0$ then $[A_1] = [A_o]$.(relabel $[A_2]$ as [A(t)]) The final expression is

$$[A(t)] = [A_o] - kt.$$

This plots as a straight line with a negative slope of k and an intercept of $[A_o]$.

First order overall, style 1

Consider the generic reaction

$$A \rightarrow B.$$

From the previous section along with knowledge that the reaction is 1st order overall, we find that

$$R = -\frac{d[A]}{dt} = k[A].$$

This can be solved for the concentration of A as a function of time.

$$\begin{aligned}
-\frac{d[A]}{dt} &= k[A] \\
-\frac{d[A]}{[A]} &= kdt \\
\frac{d[A]}{[A]} &= -kdt \\
\ln\frac{[A_2]}{[A_1]} &= -k(t_2 - t_1) \\
\frac{[A_2]}{[A_1]} &= e^{-k(t_2 - t_1)}.
\end{aligned}$$

Now if $t_1 = 0$ then $[A_1] = [A_o]$, the concentration at time zero. The final solution is an exponential decay.

$$[A(t)] = [A_o]e^{-kt}.$$

First order overall, style 2

Consider the reaction

$$aA \rightarrow B.$$

From the previous section along with knowledge that the reaction is 1st order overall, we find that

$$R = -\frac{1}{a}\frac{d[A]}{dt} = k[A].$$

This can be solved to yield the concentration of A as a function of time. I think you can already guess how this will turn out.

$$\begin{aligned} -\frac{d[A]}{dt} &= ak[A] \\ \frac{d[A]}{dt} &= -(ak)[A]. \end{aligned}$$

Now let $k_{eff} = ak$

$$\frac{d[A]}{dt} = -k_{eff}[A]$$

and the rest can be solved like before to yield

$$[A(t)] = [A_o]e^{-k_{eff}t}.$$

Other miscellaneous things, 1/e time, half life and lifetime

The lifetime of the decay is defined as $\frac{1}{k}$ or $\frac{1}{k_{eff}}$ in the second case. For the 1/e time this is where $\frac{[A(t)]}{[A(0)]} = e^{-1}$. One then finds that $kt = 1$ or $t_{\frac{1}{e}} = \frac{1}{k}$. The halflife is defined as the time it takes for one to lose half the initial population of the species of interest. This is easily determined to be

$$\begin{aligned} \frac{[A]}{[A_o]} = 0.5 &= e^{-k_{eff}t_{\frac{1}{2}}} \\ \ln(0.5) &= -k_{eff}t_{\frac{1}{2}}. \end{aligned}$$

The halflife is then

$$t_{\frac{1}{2}} = \frac{\ln(0.5)}{-k_{eff}}.$$

This is a general result.

Example

Consider the following reaction

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g).$$

The experimentally determined rate law is

$$R = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = k[N_2O_5].$$

We must integrate this equation to get the concentration (or population) of N_2O_5 as a function of time

$$-\frac{d[N_2O_5]}{[N_2O_5]} = 2kdt.$$

Integrate this to get

$$-\ln[N_2O_5] = 2kt + const$$

$$[N_2O_5] = Ae^{-2kt}$$

where $A = [N_2O_5]_0(t = 0)$. The desired solution is then

$$[N_2O_5(t)] = [N_2O_5]_0e^{-2kt}$$

which is an exponential decay.

Second order overall, style 1

A reaction is second order overall if the reaction rate is proportional to the square of the concentration of one reactant or to the product of the concentrations of two reactants

Consider the reaction

$$A \rightarrow B.$$

We know from the intro to this section and from the fact that the rate is second order overall that

$$R = -\frac{d[A]}{dt} = k[A]^2.$$

This can be solved to obtain an expression for the concentration of $[A]$ as a function of time.

$$\begin{aligned}
-\frac{d[A]}{dt} &= k[A]^2 \\
\frac{d[A]}{[A]^2} &= -kdt \\
\int \frac{d[A]}{[A]^2} &= -\int kdt \\
-\left.\frac{1}{[A]}\right|_{A_1}^{A_2} &= -k(t_2 - t_1) \\
-\frac{1}{[A_2]} + \frac{1}{[A_1]} &= -k(t_2 - t_1).
\end{aligned}$$

Now, if $t_1 = 0$ then $[A_1] = [A_o]$ and

$$-\frac{1}{[A(t)]} + \frac{1}{[A_o]} = -kt,$$

giving our final solution

$$\frac{1}{[A(t)]} = \frac{1}{[A_o]} + kt.$$

Note that a plot of $\frac{1}{[A]}$ versus t is linear. The intercept is $\frac{1}{[A_o]}$ and the slope is k.

The halflife is given by the time when $[A] = \frac{1}{2}[A_o]$

$$\begin{aligned}
\frac{1}{\frac{1}{2}[A_o]} &= \frac{1}{[A_o]} + kt \\
\frac{2}{[A_o]} - \frac{1}{[A_o]} &= kt \\
\frac{1}{[A_o]} &= kt.
\end{aligned}$$

Thus,

$$t_{\frac{1}{2}} = \frac{1}{k[A_o]}.$$

Second order overall, style 2

Consider the reaction

$$aA \rightarrow B.$$

We know from the intro to this section and from the fact that the rate is second order overall that

$$\begin{aligned} R = -\frac{1}{a}\frac{dA}{dt} &= k[A]^2 \\ -\frac{dA}{[A]^2} &= akdt \\ -\int \frac{dA}{[A]^2} &= \int akdt \\ \left.\frac{1}{[A]}\right|_{A_1}^{A_2} &= akt \\ \left(\frac{a}{[A_2]} - \frac{1}{[A_1]}\right) &= akt. \end{aligned}$$

If $t = 0$ then $[A_1] = [A_o]$ the concentration at time zero. We get

$$\frac{1}{[A(t)]} = \frac{1}{[A_o]} + akt.$$

You can see that this solution is a line with a slope of k and an intercept of $\frac{1}{A(0)}$.

Alternatively, one can rearrange the expression to get

$$[A(t)] = \frac{[A_o]}{1 + akt[A_o]}$$

where the halflife is given by

$$\begin{aligned} \frac{1}{\frac{1}{2}[A_o]} - \frac{1}{[A_o]} &= akt_{\frac{1}{2}} \\ \frac{1}{[A_o]} &= akt_{\frac{1}{2}} \end{aligned}$$

such that

$$t_{\frac{1}{2}} = \frac{1}{ak[A_o]}.$$

Second order overall, style 3

Another type of second order reaction is one that is first order in A and first order in B and thus second order overall. Note that we have an analogous style 4 where there are coefficients in front of each reactant. (maybe this is a HW problem) The generic reaction of interest is

$$A + B \rightarrow C.$$

Its experimentally determined rate law is

$$\begin{aligned} R &= k[A][B] \\ -\frac{d[A]}{dt} &= k[A][B] \end{aligned}$$

where

$$\begin{aligned} [A] &= [A_o] - x \\ &= a - x \end{aligned}$$

$$\begin{aligned} [B] &= [B_o] - x \\ &= b - x. \end{aligned}$$

With this notation change,

$$-\frac{d[A]}{dt} = \frac{dx}{dt}.$$

Putting everything together gives

$$\begin{aligned} \frac{dx}{dt} &= k(a-x)(b-x) \\ \frac{dx}{(a-x)(b-x)} &= kdt \\ \int_0^x \frac{dx}{(a-x)(b-x)} &= \int_0^t kdt \\ kt &= \int_0^x \frac{dx}{(a-x)(b-x)}. \end{aligned}$$

At this point, from a table of integrals we find

$$\int \frac{dx}{uv} = \frac{1}{k} \ln \frac{v}{u}$$

where $u = (a - x)$ and $v = (b - x)$ and $k = (b - a)$. So with regard to our problem, we get

$$\begin{aligned} kt &= \frac{1}{(b-a)} \ln(\frac{(b-x)}{(a-x)})\Big|_0^x \\ &= \frac{1}{(b-a)} \left[\ln\left(\frac{b-x}{a-x}\right) - \ln\left(\frac{b}{a}\right) \right] \\ &= \frac{1}{(b-a)} \ln \frac{a(b-x)}{b(a-x)} \end{aligned}$$

where $a = A_o$ and $b = B_o$. This gives

$$kt = \frac{1}{B_o - A_o} \ln \frac{A_o(B_o - x)}{B_o(A_o - x)}$$

where again $A_o - x = [A]$ and $B_o - x = [B]$, resulting in our final expression

$$kt = \frac{1}{[B_o - A_o]} \ln \frac{A_o[B]}{B_o[A]}.$$

As you can see life gets nasty pretty fast. What is the halflife of this process?

Reversible first order, approach 1

All of the rate laws considered so far disregard the possibility of a reverse reaction. Namely, none of them describes the overall rate close to equilibrium. This is because at equilibrium the products may be so abundant that the reverse reaction must be taken into account. As an example, consider

$$A \rightleftharpoons B$$

where the forward rate constant is k_1 and the reverse rate constant is k_{-1}. The forward and reverse rates are therefore

$$\begin{aligned} R_f &= k_1[A] \\ R_r &= k_{-1}[B]. \end{aligned}$$

Near equilibrium, the concentration of $[A]$ is reduced by the forward reaction. However, it is also replenished by the reverse reaction. The net rate of change of A is thus the sum of these two terms

$$\frac{dA}{dt} = -k_1 A + k_{-1} B.$$

Now, note that if there was never any B present initially at $t = 0$ then $A + B = A_o$ or $B = (A_o - A)$. Replace this into the above expression.

$$\begin{aligned}\frac{dA}{dt} &= -k_1 A + k_{-1}(A_o - A) \\ &= -k_1 A - k_{-1} A + k_{-1} A_o.\end{aligned}$$

To simplify things, let $k = (k_1 + k_{-1})$ and $a = k_{-1} A_o$. We get

$$\frac{dA}{dt} = -kA + a$$

which is called a linear first order non-homogeneous (does not equal zero) differential equation.

The solution to this can be assembled from the solution to the homogeneous version of the same equation along with a particular solution to the non-homogeneous part.

Homogeneous part

$$\begin{aligned}\frac{dA}{dt} &= -kA \\ \frac{dA}{A} &= -kdt \\ \ln A &= -kt + const\end{aligned}$$

giving

$$A = Ce^{-kt}$$

where C is a constant.

Particular part Assume that A is a constant. This allows us to account for the "a" term. This approach is called a trial function or otherwise known as educated guessing.

$$\begin{aligned}A &= const \\ \frac{dA}{dt} &= 0\end{aligned}$$

obviously. So now if we have

$$\begin{aligned}\frac{dA}{dt} &= -kA + a \\ 0 &= -kA + a \\ kA &= a,\end{aligned}$$

yielding the so-called particular solution

$$A = \frac{a}{k}.$$

Put both the homogeneous solution together with the particular solution

$$A = Ce^{-kt} + \frac{a}{k}.$$

At this point, we must satisfy the initial boundary condition which states that at $t = 0$ $A = A_o$.

$$A(t=0) = A_o = C + \frac{a}{k}$$

therefore

$$C = A_o - \frac{a}{k}$$

and

$$A = \left(\frac{A_o k - a}{k}\right) e^{-kt} + \frac{a}{k}.$$

Now let's consolidate the terms. Recall that $k = (k_1 + k_{-1})$ and $a = k_{-1}A_o$ to get

$$A = \frac{A_o(k_1 + k_{-1}) - k_{-1}A_o}{(k_1 + k_{-1})} e^{-(k_1+k_{-1})t} + \frac{k_{-1}A_o}{(k_1 + k_{-1})}.$$

The desired solution is then

$$\boxed{A = A_o \left[\frac{k_1 e^{-(k_1+k_{-1})t} + k_{-1}}{(k_1+k_{-1})}\right]} \tag{23.3}$$

and since $A + B = A_o$ we can find B from

$$\boxed{B = A_o \left[1 - \left[\frac{k_1 e^{-(k_1+k_{-1})t} + k_{-1}}{(k_1+k_{-1})}\right]\right]}. \tag{23.4}$$

Finally, as $t \to \infty$ we get the equilibrium value for A

$$\boxed{A_{t\to\infty} \to \frac{A_o k_{-1}}{(k_1+k_{-1})}} \tag{23.5}$$

and if $A+B = A_o$ then $B = A_o - A$, which we can use to find the equilibrium value for B

$$\boxed{B_{t\to\infty} \to A_o \left(\frac{k_1}{k_1+k_{-1}}\right)}. \tag{23.6}$$

The associated equilibrium constant for the reaction is therefore

$$K_{eq} = \frac{[B]_{eq}}{[A]_{eq}} = \left(\frac{k_1}{k_{-1}}\right).$$

But you could have already seen that at equilibrium, the forward and reverse rates equal so that

$$k_1[A] = k_{-1}[B]$$

or

$$K_{eq} = \frac{[B]}{[A]} = \left(\frac{k_1}{k_{-1}}\right).$$

Reversible first order, approach 2

Consider the reversible first order reaction

$$A \rightleftharpoons B$$

with a forward rate constant k_1 and a reverse rate constant k_2. The rate law for this reversible reaction can be written as

$$\frac{d[A]}{dt} = -k_1[A] + k_2[B].$$

Now, if the concentration of B is zero initially ($[B_o] = 0$), $[B] = [A_o] - [A]$ we get

$$\begin{aligned}
\frac{d[A]}{dt} &= -k_1[A] + k_2([A_o] - [A]) \\
&= -k_1[A] + k_2[A_o] - k_2[A] \\
&= -(k_1 + k_2)[A] + k_2[A_o] \\
&= -(k_1 + k_2)\left[[A] - \frac{k_2}{k_1 + k_2}[A_o]\right].
\end{aligned}$$

At this point, we will depart from the brute force way of solving this problem (see the last section). We recall that the equilibrium constant of the reaction is defined as

$$K_{eq} = \frac{k_1}{k_2} = \frac{[B_{eq}]}{[A_{eq}]} = \frac{[A_o] - [A_{eq}]}{[A_{eq}]}.$$

Therefore

$$\frac{[A_o]-[A_{eq}]}{[A_{eq}]}=\frac{k_1}{k_2}$$

$$[A_o]k_2-[A_{eq}]k_2=k_1[A_{eq}]$$

$$[A_o]k_2=(k_1+k_2)[A_{eq}],$$

yielding

$$[A_{eq}]=[A_o]\frac{k_2}{k_1+k_2}.$$

Use this result in the main expression where we left off to get

$$\begin{aligned}
\frac{d[A]}{dt} &= -(k_1+k_2)\left[[A]-[A_{eq}]\right] \\
\frac{d[A]}{[A]-[A_{eq}]} &= -(k_1+k_2)dt \\
\int\frac{d[A]}{[A]-[A_{eq}]} &= -\int(k_1+k_2)dt \\
\ln([A_2]-[A_{eq}])-\ln([A_1]-[A_{eq}]) &= -(k_1+k_2)(t_2-t_1).
\end{aligned}$$

If $t_1=0$ we get $[A_1]=[A_o]$. The expression then becomes

$$\ln\frac{[A]-[A_{eq}]}{[A_o]-[A_{eq}]}=-(k_1+k_2)t$$

$$\frac{[A]-[A_{eq}]}{[A_o]-[A_{eq}]}=e^{-(k_1+k_2)t}$$

$$[A]-[A_{eq}]=([A_o]-[A_{eq}])e^{-(k_1+k_2)t}$$

where $[A_o]-[A_{eq}]=\frac{k_1}{k_2}[A_{eq}]$ from the definition of the equilibrium constant. Thus,

$$[A]-[A_{eq}]=\frac{k_1}{k_2}[A_{eq}]e^{-(k_1+k_2)t}$$

$$[A] = [A_{eq}] + \frac{k_1}{k_2}[A_{eq}]e^{-(k_1+k_2)t}$$

$$[A] = [A_{eq}]\left(1 + \frac{k_1}{k_2}e^{-(k_1+k_2)t}\right)$$

and where recall that $[A_{eq}] = \frac{k_2}{k_1+k_2}[A_o]$. The desired final expression for the time dependent concentration $[A(t)]$ is therefore

$$\boxed{[A(t)] = \left(\frac{k_2[A_o]}{k_1+k_2}\right)\left(1 + \frac{k_1}{k_2}e^{-(k_1+k_2)t}\right)}. \tag{23.7}$$

What happens when $t \to \infty$? This should look familiar.

Next, we find the time dependent concentration of $[B]$. Since $[B] = [A_o] - [A]$ we find

$$\begin{aligned}
[B] &= [A_o] - [A] \\
&= [A_o] - \frac{k_2}{k_1+k_2}[A_o]\left(1 + \frac{k_1}{k_2}e^{-(k_1+k_2)t}\right) \\
&= [A_o]\left[\frac{k_1+k_2}{k_1+k_2} - \frac{k_2}{k_1+k_2}\left(1 + \frac{k_1}{k_2}e^{-(k_1+k_2)t}\right)\right] \\
&= [A_o]\left[\frac{k_1+k_2}{k_1+k_2} - \frac{k_2}{k_1+k_2} - \frac{k_1 e^{-(k_1+k_2)t}}{k_1+k_2}\right] \\
&= [A_o]\left[\frac{k_1}{k_1+k_2} - \frac{k_1}{k_1+k_2}e^{-(k_1+k_2)t}\right].
\end{aligned}$$

This results in our desired final expression for $[B(t)]$

$$\boxed{[B(t)] = \frac{k_1[A_o]}{k_1+k_2}[1 - e^{-(k_1+k_2)t}]}. \tag{23.8}$$

What happens when $t \to \infty$? This should look familiar.

Consecutive elementary reactions

Some reactions proceed through the formation of an intermediate (I) as seen in the following consecutive reaction

$$A \to I \to P$$

with a first rate constant k_a and a second rate constant k_b. More specifically, one could consider a radioactive decay process such as

$$U(239) \to Np(239) \to Pu(239).$$

We will get back to this "elementary" terminology in a moment.

To determine the way in which the concentrations of the substances in such a mechanism depend on time, the rate equations are first written down for each species. It is then necessary to obtain the solutions of these simultaneous differential equations.

Variations of the concentrations with time: The rate of decomposition of A is

$$-\frac{d[A]}{dt} = k_a[A].$$

The rate of forming I is

$$\frac{d[I]}{dt} = k_a[A] - k_b[I].$$

Likewise, the rate of forming P is

$$\frac{d[P]}{dt} = k_b[I].$$

At $t = 0$ we have the initial conditions

- $[A_o]$ is the initial concentration of A
- $[I] = 0$
- $[P] = 0$

To begin, we solve the first equation to get

$$\boxed{[A(t)] = [A_o]e^{-k_a t}}. \tag{23.9}$$

Note that this is an exponential decay. Next, we substitute this into the second equation to get

$$\begin{aligned} \frac{d[I]}{dt} &= k_a[A_o]e^{-k_a t} - k_b[I] \\ I^{'} + k_b[I] &= k_a[A_o]e^{-k_a t}. \end{aligned}$$

We re-write this in simpler notation as

$$I^{'} + k_b I = Ce^{-k_a t}$$

where $C = k_a[A_o]$.

This is a 1st order non-homogeneous linear differential equation. We will solve it via the integrating factor route. (Look back to our math interlude) Here $p(t) = k_b$ and $r(t) = Ce^{-k_a t}$ The generic solution for some function y using integrating factors is found to be

$$y = e^{-\int p dx} \left[\int e^{\int p dx} r(x) dx + const \right].$$

So in our specific case, we get for I

$$\begin{aligned} I &= e^{-k_b t} \left[\int e^{k_b t} r(t) dt + const \right] \\ &= e^{-k_b t} \left[\int C e^{k_b t} e^{-k_a t} dt + const \right] \\ &= e^{-k_b t} \left[\int C e^{k_b - k_a} t dt + const \right] \\ &= e^{-k_b t} \left[\frac{C e^{(k_b - k_a)t}}{(k_b - k_a)} + const \right] \\ &= \frac{C e^{-k_a t}}{(k_b - k_a)} + const e^{-k_b t} \end{aligned}$$

where $C = k_a[A_o]$. This gives the general solution

$$[I] = \frac{k_a[A_o] e^{-k_a t}}{(k_b - k_a)} + C_1 e^{-k_b t}.$$

We can determine what C_1 is through the constraint that $I(t = 0) = 0$

$$I(t = 0) = \frac{k_a[A_o]}{(k_b - k_a)} + C_1 = 0.$$

Therefore

$$C_1 = -\frac{k_a[A_o]}{(k_b - k_a)}.$$

Putting it all together, we get the final desired solution for $[I(t)]$

$$\boxed{[I(t)] = \frac{k_a[A_o]}{(k_b - k_a)} \left(e^{-k_a t} - e^{-k_b t} \right)} \tag{23.10}$$

Finally, we can find out what $[P]$ is because at all times, $[A]+[I]+[P]=[A_o]$. Thus

$$\begin{aligned}
[P] &= [A_o]-[A]-[I] \\
&= [A_o]-[A_o]e^{-k_at}-\frac{k_a[A_o]}{(k_b-k_a)}\left(e^{-k_at}-e^{-k_bt}\right) \\
&= [A_o]\left[1-e^{-k_at}-\frac{k_a}{(k_b-k_a)}(e^{-k_at}-e^{-k_bt})\right] \\
&= [A_o]\left[1-e^{-k_at}-\frac{k_a}{(k_b-k_a)}e^{-k_at}+\frac{k_a}{(k_b-k_a)}e^{-k_bt}\right] \\
&= [A_o]\left[1+\frac{k_a}{(k_b-k_a)}e^{-k_bt}-\left(\frac{k_b-k_a-k_a}{k_b-k_a}\right)e^{-k_at}\right] \\
&= [A_o]\left[1+\frac{k_ae^{-k_bt}}{(k_b-k_a)}-\frac{k_be^{-k_at}}{(k_b-k_a)}\right]
\end{aligned}$$

Our final expression for $[P(t)]$, the time-dependent product concentration, is therefore

$$\boxed{[P(t)]=[A_o]\left[1+\frac{(k_ae^{-k_bt}-k_be^{-k_at})}{(k_b-k_a)}\right]}. \tag{23.11}$$

Note that you could also do this by integrating $\frac{dP}{dt}=k_bI$ given that you have $I(t)$. You can do this on your own. You should get the same answer.

Parallel reactions

Here we have two parallel reactions of the initial reactant. Consider the simultaneous reactions

$$\begin{aligned}
A &\rightarrow B(\text{with a rate constant, } k_1) \\
A &\rightarrow C(\text{with a rate constant, } k_2).
\end{aligned}$$

We solve this as follows.

The rate equation for A is

$$\begin{aligned}
\frac{d[A]}{dt} &= -k_1[A]-k_2[A] \\
&= -(k_1+k_2)[A] \\
\frac{d[A]}{[A]} &= -(k_1+k_2)dt.
\end{aligned}$$

This leads to the final expression for $A(t)$

$$\boxed{[A(t)] = [A_o]e^{-(k_1+k_2)t}}. \tag{23.12}$$

Next, the rate equation for B is

$$\begin{aligned} \frac{d[B]}{dt} &= k_1[A] \\ \frac{d[B]}{dt} &= k_1[A_o]e^{-(k_1+k_2)t}, \end{aligned}$$

which is integrated to obtain

$$[B] = -\frac{k_1[A_o]}{k_1+k_2}e^{-(k_1+k_2)t} + const.$$

Now, if at $t = 0$ we have $[B] = 0$ we can find the constant of integration

$$const = \frac{k_1}{k_1+k_2}[A_o].$$

We put all of this together to get our final expression for $B(t)$

$$\boxed{[B(t)] = \tfrac{k_1[A_o]}{k_1+k_2}\left[1 - e^{-(k_1+k_2)t}\right]}. \tag{23.13}$$

Finally, the rate equation for C is

$$\begin{aligned} \frac{d[C]}{dt} &= k_2[A] \\ &= k_2[A_o]e^{-(k_1+k_2)t}. \end{aligned}$$

We integrate this to get

$$[C] = -\frac{k_2[A_o]}{k_1+k_2}e^{-(k_1+k_2)t} + const.$$

Next, if we look at the initial conditions, we notice that at $t = 0$, $[C] = 0$. This allows us to find the value of the integration constant giving

$$const = \frac{k_2[A_o]}{(k_1+k_2)}.$$

We put it all together now to get our desired final expression for $[C(t)]$

$$[C(t)] = \frac{k_2[A_o]}{(k_1+k_2)}\left[1 - e^{-(k_1+k_2)t}\right]. \tag{23.14}$$

It's apparent from these equations that the ratio of concentrations of B and C is always given by $\frac{k_1}{k_2}$ which is referred to as the branching ratio.

Temperature

As noted earlier, the rate of a reaction (in particular, the rate constant) depends on temperature. In most cases, the rate will increase with temperature. Consider the following reaction

$$NO(g) + Cl_2(g) \rightarrow NOCl(g) + Cl(g).$$

The rate constant for this reaction at 25 °C is

$$k_{25C} = 4.9 \times 10^{-6} L/mols.$$

But at 35 °C the rate constant becomes

$$k_{35C} = 1.5 \times 10^{-5} L/mols.$$

Explanation of the temperature dependence

This will lead to the empirical Arrhenius equation first developed in 1889. A collision theory picture of reactions assumes that reactants must collide with some energy greater than a minimum value and with the proper orientation for the reaction to proceed. This minimum collision energy for the reaction to occur is called the activation energy ϵ_a.

In collision theory, the rate constant, k, for a reaction is given as a product of 3 factors $k = zfp$ where

- $z \rightarrow$ collision frequency
- $f \rightarrow$ fraction of collisions with $\epsilon > \epsilon_a$
- $p \rightarrow$ fraction of collisions with correct orientation.

Here $f = e^{-\frac{\epsilon_a}{RT}}$. One then finds that

$$\boxed{k = Ae^{\frac{-\epsilon_a}{RT}}} \tag{23.15}$$

which is referred to as the Arrhenius equation after Svante Arrhenius. The symbol A is related to (pz) and is called the frequency factor. This factor has a slight temperature dependence but it is usually not huge and can be ignored.

Next, if

$$\begin{aligned} k &= Ae^{\frac{-\epsilon_a}{RT}} \\ \ln k &= \ln A - \frac{\epsilon_a}{RT} \end{aligned}$$

A plot of $\ln k$ versus $\frac{1}{T}$ then gives ϵ_a from the slope. Such a plot is called (what else)-an Arrhenius plot.

Alternatively, you can express things a little differently to find the activation energy. Take the temperature derivative of the last expression.

$$\frac{d\ln k}{dT} = \frac{\epsilon_a}{RT^2}$$

giving

$$\boxed{\epsilon_a = RT^2 \tfrac{d\ln k}{dT}}. \tag{23.16}$$

This is another expression for the activation energy.

Example

The rate constants for the formation of HI

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

at two different temperatures are (both are forward rate constants)

$$\begin{aligned} k_1 &= 2.7 \times 10^{-4} L/mols (T = 600K) \\ k_2 &= 3.5 \times 10^{-3} L/mols (T = 650K). \end{aligned}$$

Find the activation energy ϵ_a

Ans:

$$\begin{aligned} k_1 &= Ae^{\frac{-\epsilon_a}{R(600)}} \\ k_2 &= Ae^{\frac{-\epsilon_a}{R(650)}}. \end{aligned}$$

Then

$$\begin{aligned} \frac{k_1}{k_2} &= \frac{e^{\frac{-\epsilon_a}{R(600)}}}{e^{\frac{-\epsilon_a}{R(650)}}} \\ &= e^{-\frac{\epsilon_a}{R}\left(\frac{1}{600}-\frac{1}{650}\right)} \\ \ln\frac{k_1}{k_2} &= -\frac{\epsilon_a}{R}\left(\frac{1}{600}-\frac{1}{650}\right) \\ \ln\frac{2.7\times 10^{-4}}{3.5\times 10^{-3}} &= \frac{-\epsilon_a}{8.314}\left(\frac{1}{600}-\frac{1}{650}\right). \end{aligned}$$

(Does this formula look familiar?) This yields

$$\epsilon_a = 1.66 \times 10^5 J.$$

Example

Acetaldehyde CH_3CHO decomposes when heated as follows

$$CH_3CHO(g) \rightarrow CH_4(g) + CO(g).$$

The forward rate constant at two different temperatures is

$$\begin{aligned} k_{759} &= 1.05 \times 10^{-3} 1/\sqrt{M} s \\ k_{836} &= 2.14 \times 10^{-2} 1/\sqrt{M} s. \end{aligned}$$

What is the activation energy for this decomposition process?

Ans:

$$\begin{aligned} k_1 &= A e^{\frac{-\epsilon_a}{RT_1}} \\ k_2 &= A e^{\frac{-\epsilon_a}{RT_2}}. \end{aligned}$$

The ratio of the two rate constants is then

$$\begin{aligned} \frac{k_1}{k_2} &= \frac{e^{\frac{-\epsilon_a}{RT_1}}}{e^{\frac{-\epsilon_a}{RT_2}}} \\ &= e^{-\frac{\epsilon_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} \\ \ln\frac{k_1}{k_2} &= -\frac{\epsilon_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \\ \ln\frac{1.05 \times 10^{-3}}{2.14 \times 10^{-2}} &= \frac{-\epsilon_a}{8.314}\left(\frac{1}{759}-\frac{1}{836}\right). \end{aligned}$$

Solving for the activation energy, we get

$$\epsilon_a = 2 \times 10^5 J.$$

Elementary reactions

The overall chemical reactions seen previously hide information. Though simple in appearance, what happens at the molecular level might be more involved. In this respect, the overall reaction might be the result of several steps.

For example, the reaction

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

is thought to take place in 2 steps (called elementary reactions)

$$\begin{aligned} NO_2 + NO_2 &\rightarrow NO_3 + NO \\ NO_3 + CO &\rightarrow NO_2 + CO_2 \end{aligned}$$

with NO_3 as a reaction intermediate.

When dealing with elementary reactions, **the rate is proportional to the product of the concentrations of each reactant molecule**.
Example,

$$A \rightarrow B + C.$$

The rate is

$$Rate = k[A].$$

Example

$$A + B \rightarrow C + B$$

The rate is

$$Rate = k[A][B].$$

Example

$$A + B + C \rightarrow D + E$$

The rate is

$$Rate = k[A][B][C].$$

Thus any overall reaction that you see is likely to consist of several elementary steps. This is why you cannot predict the rate law by looking at the overall reaction equation.

Definition: The *molecularity* of an elementary reaction is the number of molecules coming together to react in an elementary reaction. It can be unimolecular, bimolecular etc...

Rate law and the underlying mechanism

Let's illustrate why the actual mechanism of a reaction cannot be observed directly from its overall equation.
As an example, take the overall reaction

$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g).$$

If you follow the rate of disappearance of F_2, you observe that it is directly proportional to $[NO_2]$ and $[F_2]$. The experimentally determined rate is therefore

$$R = k[NO_2][F_2].$$

Assume now that the underlying elementary reaction is

$$NO_2 + NO_2 + F_2 \rightarrow NO_2F + NO_2F.$$

But from this elementary reaction, the associated rate is

$$R = k[NO_2]^2[F_2].$$

This, however, does correspond to what is seen in the experiment so the hypothesized mechanism must be wrong.

In fact, the reaction of NO_2 with F_2 is believed to occur through the following set of reactions. The first step is called a rate determining step (i.e. a slow first step) and as its name suggests, it will control the overall reaction kinetics seen.

$$\begin{aligned} NO_2 + F_2 &\rightarrow NO_2F + F(\text{slow, rate constant, } k_1) \\ F + NO_2 &\rightarrow NO_2F(\text{fast, rate constant, } k_2). \end{aligned}$$

From these two elementary reaction, we get the overall reaction

$$2NO_2 + F_2 \rightarrow 2NO_2F.$$

Since the first step happens to be slow and is called the rate determining step, the second reaction doesn't really factor into the overall behavior of the reaction. As far as we are concerned, once the first reaction occurs, the second one happens immediately. Thus, the overall predicted reaction rate is

$$R = k_1[NO_2][F_2]$$

and matches the experimentally determined rate law.

It's apparent that when dealing with elementary steps, things can get complicated pretty fast. A reaction scheme with many steps is nearly always unsolvable analytically. One way around this problem is to use a computer to get the answer numerically. Alternatively, people sometimes make approximations that lead to analytical solutions. There are a number of approaches used to simplify life, which we describe below. These approximation techniques include

- Rate determining step
- The steady state approximation
- The rapid equilibrium approximation

We will see examples of these approximations in what follows.

Rate determining step

Suppose that for the consecutive reaction seen earlier

$$A \rightarrow I \rightarrow P$$

we have $k_b \gg k_a$ or basically that k_a is small and the first step is slow. Recall from our previous discussion about consecutive reactions that the solution for the time-dependent product concentration was

$$[P(t)] = [A_o]\left[1 + \frac{k_a e^{-k_b t} - k_b e^{-k_a t}}{(k_b - k_a)}\right].$$

Now since $k_b \gg k_a$ we can drop a few terms in the above expression.

$$[P(t)] \simeq [A_o]\left[1 - \frac{k_b e^{-k_a t}}{k_b}\right].$$

Thus, we get our final approximate expression

$$\boxed{[P(t)] \simeq [A_o](1 - e^{-k_a t})} \tag{23.17}$$

and you can see that the product formation depends only on the slower of the two rates, (associated with k_a). Again, this slower reaction is called the rate determining step.

Alternatively, you could have seen this as follows. The first step is slow so basically you have

$$A \rightarrow P$$

Then

$$\begin{aligned} \frac{dA}{dt} &= -k_a A \\ A &= A_o e^{-k_a t} \end{aligned}$$

where $A + P = A_o$ so $P = A_o - A$ and

$$P = A_o - A_o e^{-k_a t}$$
$$\boxed{P = A_o\left(1 - e^{-k_a t}\right)}.$$

Example, rate determining step (slow 1st step, fast 2nd step)

Determine the rate law from a mechanism with an initial slow step. The overall reaction equation is

$$O_3(g) + 2NO_2(g) \rightarrow O_2(g) + N_2O_5(g).$$

The proposed mechanism in terms of elementary reactions is

$$\begin{aligned} O_3 + NO_2 &\rightarrow NO_3 + O_2(\text{slow}) \\ NO_3 + NO_2 &\rightarrow N_2O_5(\text{fast}) \end{aligned}$$

where NO_3 is an intermediate. What is the rate law predicted by this mechanism?

Ans: The rate determining step is

$$O_3 + NO_2 \rightarrow NO_3 + O_2$$

such that the predicted rate is

$$R \propto k[O_3][NO_2]$$

and this should hopefully match the experimentally observed rate law.

Example, rate determining step (slow 1st step, fast 2nd step)

The iodide ion catalyzed decomposition of hydrogen peroxide H_2O_2 is believed to follow the mechanism

$$\begin{aligned} H_2O + I^- &\rightarrow H_2O + IO^- (\text{slow, rate constant, } k_1) \\ H_2O_2 + IO^- &\rightarrow H_2O + O_2 + I^- (\text{fast, rate constant, } k_2) \end{aligned}$$

with IO^- and I^- acting as intermediates. The overall reaction is

$$2H_2O_2 \rightarrow 2H_2O + O_2.$$

What is the rate law predicted by this mechanism?

Ans:

$$R = k_1[H_2O][I^-]$$

since the 1st step is the rate determining step.

The steady state approximation

The second of our life-improving approximations is the steady state approximation. This approximation says that the rate of change of all *intermediates* in the reaction is zero after some finite induction time.

Steady state approximation, style 1

Consider one such reaction, which we have previously seen

$$A \rightarrow I \rightarrow P$$

with rate constants k_a and k_b for the first and second steps respectively. Recall that I is an intermediate here.

Let's write down the different rates for each species.

$$\begin{aligned} \frac{dA}{dt} &= -k_a A \\ \frac{dI}{dt} &= k_a A - k_b I \\ \frac{dP}{dt} &= k_b I. \end{aligned}$$

This time, invoke the steady state approximation which says that $\frac{dI}{dt} = 0$ if we wait long enough. Thus

$$k_a[A] = k_b[I]$$

or

$$[I] = \frac{k_a}{k_b}[A].$$

Plug this result into $\frac{dP}{dt} = k_b[I]$ to get

$$\frac{dP}{dt} = k_b \frac{k_a}{k_b}[A] = k_a[A].$$

We know from solving the first order equation for A that $[A] = [A_o]e^{-k_a t}$. As a consequence,

$$\frac{dP}{dt} = k_a[A_o]e^{-k_a t}$$

which we integrate to get

$$\begin{aligned} [P] &= k_a[A_o] \left. \frac{e^{-k_a t}}{-k_a} \right|_0^t \\ &= -[A_o]\left(e^{-k_a t} - 1\right). \end{aligned}$$

This is our final result for the time dependent population of the product

$$\boxed{[P(t)] = [A_o]\left(1 - e^{-k_a t}\right)}. \tag{23.18}$$

Notice that this result is the same as that from the rate determining step approximation (look back to previous section) which results when $k_b \gg k_a$.

Steady state approximation, style 2

Consider the following reaction where now we include reversible steps

$$A \rightleftharpoons I \rightleftharpoons B.$$

Obviously, things get more complicated. But the claim is that invoking the steady state approximation will simplyf life. Let's see. In the reaction, the first forward and reverse rate constants are k_1 and k_{-1} respectively. The second forward and reverse rate constants are k_2 and k_{-2}. We now write down the rates for each species

$$\begin{aligned} \frac{d[A]}{dt} &= -k_1[A] + k_{-1}[I] \\ \frac{d[I]}{dt} &= k_1[A] - k_{-1}[I] - k_2[I] + k_{-2}[B] \\ \frac{d[B]}{dt} &= k_2[I] - k_{-2}[B]. \end{aligned}$$

Using the steady state approximation, we now set $\frac{d[I]}{dt} = 0$

$$\frac{d[I]}{dt} = k_1[A] - (k_{-1} + k_2)[I] + k_{-2}[B] = 0.$$

Therefore

$$(k_{-1} + k_2)[I] = k_1[A] + k_{-2}[B]$$

or that

$$\boxed{[I] = \tfrac{k_1[A]+k_{-2}[B]}{(k_{-1}+k_2)}}. \tag{23.19}$$

Substitute this result into equations 1 and 3.
First $[A]$

$$\begin{aligned}
\frac{d[A]}{dt} &= -k_1[A] + \frac{k_{-1}(k_1[A] + k_{-2}[B])}{(k_{-1} + k_2)} \\
&= -k_1[A] + \frac{k_1k_{-1}}{(k_{-1} + k_2)}[A] + \frac{k_{-1}k_{-2}[B]}{(k_{-1} + k_2)} \\
&= -k_1[A]\left[1 - \frac{k_{-1}}{(k_{-1} + k_2)}\right] + \frac{k_{-1}k_{-2}}{(k_{-1} + k_2)} \\
&= -k_1[A]\left[\frac{k_{-1} + k_2 - k_{-1}}{(k_{-1} + k_2)}\right] + \frac{k_{-1}k_{-2}}{(k_{-1} + k_2)}[B],
\end{aligned}$$

giving our desired expression for $[A]$

$$\frac{d[A]}{dt} = -\frac{k_1k_2}{(k_{-1} + k_2)}[A] + \frac{k_{-1}k_{-2}}{(k_{-1} + k_2)}[B].$$

Next $[B]$

$$\begin{aligned}
\frac{d[B]}{dt} &= \frac{k_2}{(k_{-1} + k_2)}(k_1[A] + k_{-2}[B]) - k_{-2}[B] \\
&= \frac{k_1k_2}{(k_{-1} + k_2)}[A] + \frac{k_2k_{-2}}{(k_{-1} + k_2)}[B] - k_{-2}[B] \\
&= \frac{k_1k_2}{(k_{-1} + k_2)}[A] - k_{-2}[B]\left(1 - \frac{k_2}{(k_{-1} + k_2)}\right) \\
&= \frac{k_1k_2}{(k_{-1} + k_2)}[A] - k_{-2}[B]\left(\frac{k_{-1} + k_2 - k_2}{(k_{-1} + k_2)}\right),
\end{aligned}$$

yielding the desired expression for B

$$\frac{d[B]}{dt} = \frac{k_1 k_2}{(k_{-1}+k_2)}[A] - \frac{k_{-1}k_{-2}}{(k_{-1}+k_2)}[B].$$

Now, given that we have eliminated the intermediate, put the remaining two equations together. To simplify things, let

$$\begin{aligned} k_f &= \frac{k_1 k_2}{(k_{-1}+k_2)} \\ k_r &= \frac{k_{-1}k_{-2}}{(k_{-1}+k_2)} \end{aligned}$$

be effective forward and reverse rates. Our two equations for A and B therefore become

$$\begin{aligned} \frac{d[A]}{dt} &= -k_f[A] + k_r[B] \\ \frac{d[B]}{dt} &= k_f[A] - k_r[B]. \end{aligned}$$

This clearly reduces the entire problem to a standard reversible 1st order reaction

$$A \rightleftharpoons B,$$

which we have already solved previously, provided certain initial condition constraints.

Pre-equilibrium, style 1

Let's now take a look at the third approximation that will simplify life. Consider the reaction

$$A \rightleftharpoons I \rightarrow B$$

with initial forward and reverse rate constants k_1 and k_{-1} respectively and a second rate constant k_2. Furthermore assume that $k_{-1} \gg k_2$ such that a pre-equilibrium is established between A and I.

Now, if a pre-equilibrium is established we ignore B and recognize that what we effectively have is $A \rightleftharpoons I$. At equilibrium, the corresponding forward and reverse rates equal, giving

$$k_1[A] = k_{-1}[I].$$

Then

$$[I] = \frac{k_1}{k_{-1}}[A].$$

and this is introduced into the rate of product formation

$$\begin{aligned} R &= k_2[I] \\ &= \frac{k_1 k_2}{k_{-1}}[A]. \end{aligned}$$

Let $k_{eff} = \frac{k_1 k_2}{k_{-1}}$ giving

$$R = k_{eff}[A].$$

Finally, we get $[A]$ from the previous section where we solved for A in the $A \rightleftharpoons B$ type of reaction. In this case, we find A for $A \rightleftharpoons I$, provided certain initial condition constraints.

Pre-equilibrium, style 2

A weak complex, AB, is formed in the reaction

$$A + B \rightleftharpoons AB \rightarrow C$$

where the first forward and reverse rate constants are k_1 and k_{-1} respectively. The second rate constant is k_2. Assuming that $k_{-1} \gg k_2$ write the rate law describing the formation of C.

Ans: Assume pre-equilibrium so that the forward and reverse rates in the first step equal

$$k_1[A][B] = k_{-1}[AB].$$

We then see that

$$[AB] = \frac{k_1}{k_{-1}}[A][B].$$

The rate of formation of C is now

$$\frac{d[C]}{dt} = k_2[AB]$$

where replacing our pre-equilibrium derived expression for AB gives

$$\frac{d[C]}{dt} = \frac{k_1 k_2}{k_{-1}}[A][B].$$

Example, pre-equilibrium

Consider the overall reaction

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g).$$

This reaction has the proposed following mechanism

$$\begin{aligned} N_2O_5 &\rightleftharpoons NO_2 + NO_3(\text{fast, equilib, rate constants, } k_1 \text{ and } k_{-1}) \\ NO_2 + NO_3 &\rightarrow NO + NO_2 + O_2(\text{slow, rate constant, } k_2) \\ NO_3 + NO &\rightarrow 2NO_2(\text{fast, rate constant, } k_3). \end{aligned}$$

The experimentally determined rate law is

$$R = k[N_2O_5].$$

We will now show how the elementary rates match up to what is measured experimentally. From elementary reaction 2

$$R = k_2[NO_2][NO_3].$$

But $[NO_3]$ is an intermediate. This rate can't be compared with the experimental rate since we don't see the intermediate. Thus, our immediate goal is to eliminate $[NO_3]$ from the above expression.

From reaction 1

$$\begin{aligned} R_f &= k_1[N_2O_5] \\ R_r &= k_{-1}[NO_2][NO_3]. \end{aligned}$$

Next, once equilibrium is established the forward and reverse rates equal. Thus,

$$\begin{aligned} R_f &= R_r \\ k_1[N_2O_5] &= k_{-1}[NO_2][NO_3] \end{aligned}$$

or

$$[NO_3] = \frac{k_1[N_2O_5]}{k_{-1}[NO_2]}.$$

Substitute this into the above rate for reaction 2

$$\begin{aligned} R &= k_2[NO_2]\frac{k_1[N_2O_5]}{k_{-1}[NO_2]} \\ &= \frac{k_1k_2}{k_{-1}}\frac{[NO_2][N_2O_5]}{[NO_2]}. \end{aligned}$$

The final desired result that can be compared to the experimentally determined rate law and is

$$R = \frac{k_1 k_2}{k_{-1}}[N_2O_5].$$

You can see that it matches the experimentally rate law. Furthermore, note that the apparent rate constant is really a product of 3 microscopic rate constants.

Example, pre-equilibrium

Nitric oxide can be reduced with hydrogen gas to give nitrogen and water vapor, according to the overall reaction

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g).$$

A proposed mechanism, using elementary steps, is

$$\begin{array}{rcl} 2NO & \rightleftharpoons & N_2O_2(\text{fast, equilib, rate constants } k_1 \text{ and } k_{-1}) \\ N_2O_2 + H_2 & \rightarrow & N_2O + H_2O(\text{slow, rate constant } k_2) \\ N_2O + H_2 & \rightarrow & N_2 + H_2O(\text{fast, rate constant, } k_3). \end{array}$$

What is the rate law predicted by this mechanism?

Ans: Start with the slow rate limiting step

$$R = k_2[N_2O_2][H_2]$$

where N_2O_2 is an intermediate. Now from reaction 1 where a pre-equilibrium situation exists

$$k_1[NO]^2 = k_{-1}[N_2O_2].$$

Therefore

$$[N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$$

and our predicted rate, which can be compared to experiment, is

$$R = \frac{k_2 k_1}{k_{-1}}[NO]^2[H_2].$$

Again, one can see that the experimental rate constant is complicated and is really a product of three microscopic rate constants.

Example, pre-equilibrium

Nitric oxide, NO, reacts with oxygen to produce nitrogen dioxide via the overall reaction

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g).$$

The proposed mechanism, using elementary steps, is

$$\begin{aligned} NO + O_2 &\rightleftharpoons NO_3(\text{fast, equilibrium, rate constants } k_1 \text{ and } k_{-1}) \\ NO_3 + NO &\rightarrow NO_2 + NO_2(\text{slow, rate constant } k_2) \end{aligned}$$

Here, NO_3 is an intermediate. What is the predicted rate law for the overall reaction.

Ans: Start with the slow rate limiting step

$$R = k_2[NO_3][NO].$$

Note that NO_3 is an intermediate. Using reaction 1, we then have the following equilibrium so that

$$k_1[NO][O_2] = k_{-1}[NO_3].$$

We can therefore get an expression for $[NO_3]$ using this

$$[NO_3] = \frac{k_1}{k_{-1}}[NO][O_2].$$

When inserted into the rate of the rate limiting step, we get our predicted rate, which can be compared to the experimental rate

$$R = \frac{k_1 k_2}{k_{-1}}[NO]^2[O_2].$$

Again, the experimental rate constant is complicated as it consists of a product of three microscopic rate constants.

Some important examples

Finally, let's end this chapter with two important examples.

Case study 1: Unimolecular reactions

A number of gas phase reaction follow 1st order kinetics. The problem with this is that presumably the energy to allow the reaction comes from collisions (presumably, these are bimolecular events). So how can we see 1st order rate laws?

One mechanism was proposed by Lindemann in 1921 and was followed by work by Hinshelwood. The result today is what is known as the Lindemann-Hinshelwood mechanism. This is outlined below briefly. Consider the case where a molecule becomes excited by a collision with a fellow molecule, the excited molecule is denoted by A^*

$$A + A \rightarrow A^* + A.$$

The rate of excited state formation is

$$\frac{d[A^*]}{dt} = k_a[A]^2.$$

Now, the excited molecule could suffer a collision with a normal molecule to deactivate it

$$A + A^* \rightarrow A + A.$$

This occurs with an associated rate

$$\frac{d[A^*]}{dt} = -k_a^{'}[A][A^*].$$

Alternatively, the excited molecule can react with itself to form the product (the unimolecular step).

$$A^* \rightarrow P.$$

This occurs with a rate

$$\frac{d[A^*]}{dt} = -k_b[A^*]$$

or with a rate of product formation

$$\frac{d[P]}{dt} = k_b A^*.$$

Now, if k_b is rate limiting you will get what is effectively 1st order kinetics as seen experimentally. But this can be demonstrated more explicitly by taking the steady state approximation to A^*, the intermediate so to speak.

Putting all the formation and deactivation pathways for A^* together we get

$$\frac{d[A^*]}{dt} = k_a[A]^2 - k_{a'}[A][A^*] - k_b[A^*] = 0$$

or that

$$k_a[A]^2 = (k_a^{'}[A] + k_b)[A^*].$$

Solving for the intermediate gives

$$[A^*] = \frac{k_a[A]^2}{k_a^{'}[A] + k_b}.$$

Plug this expression into that for the rate of product formation to get

$$\begin{aligned} \frac{dP}{dt} &= k_b[A^*] \\ &= \frac{k_b k_a[A]^2}{(k_a^{'}[A] + k_b)}. \end{aligned}$$

Now, if $k_a^{'} \gg k_b$

$$\begin{aligned} \frac{dP}{dt} &\simeq \frac{k_b k_a[A]^2}{k_a^{'}[A]} \\ &\simeq \frac{k_b k_a}{k_{a'}}[A], \end{aligned}$$

leading to the final expression for the predicted rate of product formation

$$\frac{d[P]}{dt} = k_{eff}[A]$$

where $k_{eff} = \frac{k_b k_a}{k_{a'}}$, which can be compared to the actual experiment.

Case study 2: The Michaelis-Menten mechanism

This is another example of a reaction where an intermediate is formed. It describes enzyme action. In particular, the rate of an enzyme (E) catalyzed reaction in which a substrate (S) is converted to product (P) is found to depend on the concentration of (E). Experimental studies reveal that the rate law follows

$$-\frac{d[S]}{dt} = \frac{k[S]}{K + [S]}$$

where $[S]$ is the substrate concentration and k, K are constants.

The proposed mechanism to explain this rate law was derived by Leonor Michaelis and Maude Menten in 1913. Their mechanism is a 2 step process that involves the formation of an intermediate called ES. The mechanism is

$$E + S \rightleftharpoons ES \rightarrow P + E$$

with forward and reverse rate constants k_a and $k_{a'}$ respectively and the second rate constant being k_b. The intermediate is the so-called bound state ES. Before beginning our analysis note the following. The rate of product formation is

$$\frac{d[P]}{dt} = k_b[ES].$$

From the conservation of enzymes (whether free or bound),

$$E_{tot} = E + ES.$$

Now, let's begin our analysis by taking the steady state approximation. We set the rate of change of the intermediate bound state to zero

$$\begin{aligned} \frac{d[ES]}{dt} &= 0 \\ &= k_a[E][S] - k_{a'}[ES] - k_b[ES] = 0. \end{aligned}$$

Therefore,

$$k_a[E][S] = (k_{a'} + k_b)[ES].$$

Rearrange this expression to get

$$[E] = \frac{(k_{a'} + k_b)}{k_a}\frac{[ES]}{[S]}$$

so that

$$\begin{aligned} E_{tot} &= E + ES \\ &= \left(\frac{k_a' + k_b}{k_a}\right)\frac{[ES]}{[S]} + [ES]. \end{aligned}$$

Call $k_m = \left(\frac{k_{a'}+k_b}{k_a}\right)$, the Michaelis constant. This gives

$$\begin{aligned} E_{tot} &= k_m \frac{[ES]}{[S]} + [ES] \\ &= \left(\frac{k_m}{[S]} + 1\right)[ES] \end{aligned}$$

or

$$[ES] = \frac{E_{tot}}{\left(\frac{k_m}{[S]} + 1\right)}.$$

Replace this into the rate of product formation

$$\frac{d[P]}{dt} = k_b[ES]$$

to obtain the desired rate of product formation.

$$\boxed{\frac{d[P]}{dt} = \frac{k_b[E_{tot}]}{\left(\frac{k_m}{[S]}+1\right)}}. \tag{23.20}$$

Now, rearrange this equation by inverting it

$$\frac{1}{\left(\frac{d[P]}{dt}\right)} = \frac{\left(\frac{k_m}{[S]} + 1\right)}{k_b[E_{tot}]}$$

which, in turn, yields an equivalent expression

$$\frac{1}{\left(\frac{d[P]}{dt}\right)} = \frac{k_m}{k_b[S][E_{tot}]} + \frac{1}{k_b[E_{tot}]}.$$

It's apparent that you can plot 1/rate versus 1/[S] to get a straight line with a slope of $\frac{k_m}{k_b[E_{tot}]}$ and an intercept of $\frac{1}{k_b[E_{tot}]}$. Such a plot is called a Lineweaver-Burke plot.

Michaelis-Menten mechanism, style 2

Just to show you that you can make things difficult for yourself, sometimes the following is derived, which is valid for early times of the reaction.

Return to the Michaelis-Menten mechanism made slightly more general with a reversible 2nd step

$$E + S \rightleftharpoons ES \rightleftharpoons P + E.$$

The forward and reverse rate constants are k_1 and k_{-1} while the second forward and reverse rate constants are k_2 and k_{-2} respectively.

We write the explicit rates for each species.

$$\begin{aligned}\frac{d[S]}{dt} &= -k_1[E][S] + k_{-1}[ES] \\ \frac{d[ES]}{dt} &= k_1[E][S] - (k_{-1} + k_2)[ES] + k_2[E][P] \\ \frac{d[P]}{dt} &= k_2[ES] - k_{-2}[E][P].\end{aligned}$$

In all cases $E_{tot} = [ES] + [E]$ since the enzyme is not consumed by the reaction. Rearrange this to get

$$[E] = [E]_{tot} - [ES]$$

and replace this into the ES rate expression

$$\frac{d[ES]}{dt} = k_1[E]_{tot}[S] + k_{-2}[E]_{tot}[P] - [ES](k_1[S] + k_{-1} + k_2 + k_{-2}[P]).$$

Next, take the steady state approximation $\frac{d[ES]}{dt} = 0$. (remember that the implicit goal for doing this is to allow us to eliminate $[ES]$ from all other expressions). We have

$$k_1[E]_{tot}[S] + k_{-2}[E]_{tot}[P] = [ES](k_1[S] + k_{-1} + k_2 + k_{-2}[P])$$

which can get rearranged to give

$$[ES] = \frac{(k_1[S] + k_{-2}[P])[E]_{tot}}{k_1[S] + k_{-1} + k_2 + k_{-2}[P]}.$$

Shove this expression for ES back into our first equation for the rate of change of the substrate

$$\begin{aligned}\frac{d[S]}{dt} &= -k_1[E][S] + k_{-1}[ES] \\ &= -k_1[E][S] + \frac{k_{-1}(k_1[S] + k_{-2}[P])[E]_{tot}}{k_1[S] + k_{-1} + k_2 + k_{-2}[P]}.\end{aligned}$$

Here, replace [E] with $[E] = [E]_{tot} - [ES]$ using the conservation of enzyme. We get

$$\begin{aligned}\frac{d[S]}{dt} &= -k_1[S]([E]_{tot} - [ES]) + \frac{k_{-1}(k_1[S] + k_{-2}[P])[E]_{tot}}{k_1[S] + k_{-1} + k_2 + k_{-2}[P]} \\ &= -k_1[S][E]_{tot} + k_1[S][ES] + \frac{k_{-1}(k_1[S] + k_{-2}[P])[E]_{tot}}{k_1[S] + k_{-1} + k_2 + k_{-2}[P]}.\end{aligned}$$

Ok, this gets complicated. Let's consolidate all terms. First, we need a common denominator, call it stuff.

$$\text{stuff} = k_1[S] + k_{-1} + k_2 + k_{-2}[P].$$

We get

$$\frac{d[S]}{dt} = \left(\frac{-k_1[S][E]_{tot}(\text{stuff})}{(\text{stuff})} + \frac{k_1^2[S]^2[E]_{tot}}{(\text{stuff})} + \frac{k_1k_{-2}[S][P]}{(\text{stuff})} + \frac{k_1k_{-1}[S]}{(\text{stuff})}\right) + \frac{k_{-1}k_{-2}[P]}{(\text{stuff})}.$$

You can now evaluate the stuff in parenthesis (a little tedious) and find that it equals

$$-\frac{k_1k_2[S][E]_{tot}}{(\text{stuff})}.$$

So that when you put it all together you get

$$\frac{d[S]}{dt} = \left(-\frac{k_1k_2[S]}{(\text{stuff})} + \frac{k_{-1}k_{-2}[P]}{(\text{stuff})}\right)[E]_{tot}.$$

This gives our final expression for the rate of change of the substrate

$$\boxed{\frac{d[S]}{dt} = \frac{(-k_1k_2[S]+k_{-1}k_{-2}[P])[E]_{tot}}{k_1[S]+k_{-1}+k_2+k_{-2}[P]}}. \tag{23.21}$$

Now if the reaction does not progress very far (an important key assumption which simplifies the result but ultimately limits it to short times) then

- $[S] \simeq [S_o]$
- $[P] \simeq 0$

where $[S_o]$ is the initial substrate concentration. We then get

$$\begin{aligned} \frac{d[S]}{dt} &= -\frac{k_1 k_2 [S_o][E]_{tot}}{k_1[S_o] + k_{-1} + k_2} \\ &= -\frac{k_2[S_o][E]_{tot}}{[S_o] + \left(\frac{k_{-1}+k_2}{k_1}\right)}. \end{aligned}$$

Now, let $k_m = \frac{k_{-1}+k_2}{k_1}$ which is the Michaelis constant. The final expression we have for the rate of change of the substrate is then

$$\boxed{\frac{d[S]}{dt} = -\frac{k_2[S_o][E]_{tot}}{k_m+[S_o]}}. \tag{23.22}$$

Notice that this is virtually identical to the previous expression except that we have made an early time assumption so that $[E] \to [E_o]$. Otherwise they are identical. The above equation also shows that the initial rate for an enzyme catalyzed reaction is

- first order at low substrate concentration ($k_m \gg [S_o]$)
- zeroth order at high substrate concentration ($k_m \ll [S_o]$)

Finally, we can get some more information from this expression. At high substrate concentration conditions

$$\frac{d[S]}{dt} = -k_2[E]_{tot} = R_{max}$$

and is the maximum rate of the Michaelis-Menten mechanism. Next, the turnover number is defined as R_{max}/conc. of enzyme active sites. This is the maximum number of substrate molecules converted to product per unit time. If the enzyme has a single active site, the concentration of active sites equals $[E]_{tot}$. Therefore the turnover number is

$$\text{turnover-number} = \frac{R_{max}}{[E]_{tot}} = \frac{k_2[E]_{tot}}{[E]_{tot}} = k_2.$$

Inhibitors

The ability of enzymes to catalyze reactions can be hindered by inhibitor molecules. One of the mechanisms by which an inhibitor works is by competing with the substrate for binding to the active site of the enzyme. We can include this inhibition reaction in a modified Michaelis-Menten mechanism for enzyme catalysis. Let's do it and see what we get.

The standard enzyme substrate reaction is

$$E + S \rightleftharpoons ES$$

with forward and reverse reaction rates, k_1 and k_{-1} respectively. Now, we have the inhibitor (I) reaction that interferes with the above reaction

$$E + I \rightleftharpoons EI.$$

It produces an inhibitor-enzyme complex, EI with forward and reverse rate constants k_2 and k_{-2}. Finally, we have the product forming reaction

$$ES \rightarrow E + P$$

with a rate constant k_3.

We now determine the rate laws for all the species, $[S]$, $[ES]$, $[EI]$, and $[P]$.

$$\begin{aligned}
\frac{d[EI]}{dt} &= k_2[E][I] - k_{-2}[EI] \\
\frac{d[S]}{dt} &= -k_1[E][S] + k_{-1}[ES] \\
\frac{d[ES]}{dt} &= k_1[E][S] - (k_{-1} + k_3)[ES] \\
\frac{d[P]}{dt} &= k_3[ES].
\end{aligned}$$

To simplify things, consider the case where the 1st and 3rd reactions are always in equilibrium.

For the first equation we find at equilibrium that the forward and reverse rates equal

$$k_2[E][I] = k_{-2}[EI]$$

or that

$$\frac{[EI]_{eq}}{[E]_{eq}[I]_{eq}} = \frac{k_2}{k_{-2}} = K_{eq}.$$

From this, we get

$$[EI]_{eq} = K_{eq}[E]_{eq}[I]_{eq}.$$

Next, for the third equation we get

$$k_1[E][S] = (k_{-1} + k_3)[ES]$$

such that

$$[ES] = \frac{[E][S]}{k_m}$$

where $k_m = \frac{k_{-1}+k_3}{k_1}$. Use this expression as a means of getting rid of this intermediate in the other rate equations.

Now the rate of product formation is

$$\frac{d[P]}{dt} = k_3[ES]$$

where $[ES] = \frac{[E][S]}{k_m}$. So we get

$$\frac{d[P]}{dt} = k_3\frac{[E][S]}{k_m}.$$

At this point, we aim to get rid of $[E]$ in this expression. We can do this by realizing that the amount of enzyme is conserved

$$\begin{aligned} [E]_o &= [E] + [ES] + [EI] \\ &= [E] + \frac{[E][S]}{k_m} + K_{eq}[E][I]. \end{aligned}$$

This leads to an expression for $[E]$

$$[E] = \frac{[E_o]}{1 + \frac{[S]}{k_m} + K_{eq}[I]},$$

which we use in our main expression for the rate of product formation.

$$\begin{aligned} \frac{d[P]}{dt} &= k_3\frac{[E_o][S]}{k_m\left(1 + \frac{[S]}{k_m} + K_{eq}[I]\right)} \\ &= \frac{k_3[E_o][S]}{(k_m + [S] + k_m K_{eq}[I])}. \end{aligned}$$

Finally, let $k^{'} = k_m(1 + K_{eq}[I])$ to get our desired expression

$$\boxed{\frac{d[P]}{dt} = \frac{k_3[E_o][S]}{k^{'}+[S]}}. \qquad (23.23)$$

At short times, $[S] \simeq [S_o]$ and we get

$$\boxed{\frac{d[P]}{dt} = \frac{k_3[E_o][S_o]}{k^{'}+[S_o]}}. \qquad (23.24)$$

Finally, if there is no inhibitor present $[I] = 0$ and $k^{'} = k_m$. This returns us to the original Michaelis-Menten equation.

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