

Thermodynamics

State and Path Functions

- A **state function** is one whose value depends **only on the state of the substance** under consideration – no matter how that state was arrived at.
- The value of **path functions** depends on the path which the system takes in arriving to that particular state.
- The quantities in this course are as follows:

State	Path
U	
(Evidence: can't make a perpetual motion machine)	q
H	w
S	
G	

- The **sign convention** is such that **positive values** correspond to things **done onto**, or **absorbed into, the system**.

Gas laws

- An **ideal gas** has the following equation of state:

$$\boxed{pV = nRT}$$

This is assuming that the gas is composed of molecules that do not interact significantly with one another and are negligibly small compared to the space between the molecules.

The First Law

- The **First Law of Thermodynamics** states that **energy cannot be created or destroyed – it is just transformed from one form into another**.
- The **internal energy** of an object is a **property of matter** – a measure of the “energy reserves” of the system.
- The first law can be expressed as

$$\boxed{\Delta U = q + w}$$

Where w and q are the **heat absorbed** and **work done on** the system respectively.

- The **internal energy** is the total energy possessed by the system – it is the sum of kinetic and potential energies of the system.
- At **constant volume**, the work done on the surroundings is clearly 0, since no expansion happens. So:

$$\boxed{\Delta U = q} \quad (\text{constant volume})$$

- We define the quantity **enthalpy** as follows:

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

- Now, consider a process at **constant pressure**. In such a case, $\Delta U = \delta w + \delta q$, but $\delta w = -p_{\text{ext}}\Delta V$. This means that

$$\boxed{\Delta H = q} \quad (\text{constant pressure})$$

- When we put heat into an object, its temperature increases. The relationship is

$$q = C\Delta T$$

Since, at constant volume, $\Delta U = \delta q$, then C takes the value

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V}$$

At constant pressure, however, it is $\Delta H = \delta q$ that holds, so C takes the value

$$\boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P}$$

These allow to convert values for H and U from one temperature to another.

The Second Law

- Some processes are **spontaneous**, some not. A **spontaneous process** is one that, once started, can take place without any further intervention.
- The **second law of thermodynamics** states that **in a spontaneous process, the entropy of the universe increases**. At equilibrium, the **change in entropy** of the universe is **0**.
- The molecular definition of entropy

- If we assume that a given system has no particular preference for any given energy configuration, then it is the one with the greatest number of arrangements (W) which will exist. The **Boltzmann Distribution** gives this as

$$n_i = n_0 e^{-\varepsilon_i/kT}$$

Where n_i is the number of molecules in energy level i , with energy ε_i , and the lowest energy level has $i = 0$, with energy 0.

- Boltzmann postulated that entropy is related in the number of ways a distribution can be achieved

$$S = k \ln W$$

Examples:

- When **heating** a system, the molecules have more energy and therefore move up to higher energy levels [cf. Boltzmann Distribution]. There are therefore more ways of achieving the resulting distribution, and *the entropy increases*. The change, however, is **greater at lower temperatures**.
 - When **expanding** a system, Quantum Mechanics tell us that the spacing of the energy levels decreases. There are therefore more energy levels within kT of the ground state available, and W therefore increases, so *the entropy increases*.
 - Increase from a solid to a liquid to a gas is also associated with a large increase in the number of energy levels, because of greater spatial freedom.
- The “classical” definition of entropy
 - We define a **change** in entropy in the following way:

$$dS = \frac{\delta q_{rev}}{T}$$

Where T is the temperature of the object and δq_{rev} is the amount of heat **absorbed** by the object **reversibly**.

- Essential points to note are as follows:
 - This involves the change in **heat**, not in work – this makes sense, given that work is the orderly transfer of work, whereas heat is the disorderly transfer of work, and entropy is related to disorder.
 - This definition involves the heat change of a process **when it happens reversibly** – in other words, in such a way that an infinitesimal change in a variable can reverse the direction of the process.¹ *Mechanical reversibility* refers to the equality of pressure. *Thermal*

¹ Note: I have a feeling that’s what happening is as follows. Since entropy is a state function, all we really want to know is the change from one given state to another, regardless of the way it happens. Reversible heat transfer is smooth, careful and restrained. It ensures that no “hot spots” [or the equivalent] are created which will later spontaneously dissipate and add to the entropy. Using a non-reversible heat change would result in a lower value for dS , but to a state which isn’t the “final one” since entropy remains to be dissipated.

reversibility refers to equality in temperature. Reversible processes are:

- Infinitely slow
- At equilibrium
- Do maximum work
- The presence of temperature in the denominator reflects the fact that an increase in heat has a greater effect at a lower temperature.
- We usually split the universe into the **system** and the **surroundings**. The entropy change of the surroundings is given by

$$\boxed{dS_{surr} = -\frac{\delta q_{sys}}{T}}$$

Notes:

- This is because we assume that the system is **closed** – the only thing exchanged between the system and the surroundings is **heat**. As such, the entropy change of the surroundings is simply as a result of gain or loss of heat.
- Furthermore, if the **system absorbs** energy δq_{sys} , then the surroundings **absorb** energy $-\delta q_{sys}$.
- The surroundings are so large that we assume T does not change as this energy is gained or lost from the surroundings.
- Finally, we note that we do **not** need this heat change to be reversible because *any* heat exchanged with the system can be considered as reversible from the point of view of the surroundings. This is because, since the surroundings are so large, their pressure stays constant and $\delta q_{surr} = \Delta H_{surr}$. Since H is a state function, q_{surr} must be the same whatever way it is absorbed.
- For **constant pressure** processes, we know that $\delta q = dH$, so

$$dS = \frac{dH}{T}$$

Using our definition of C_P , we can write

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

We can use this in two ways:

- To find absolute entropies

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

$$\int_0^{T^*} dS = \int_0^{T^*} \frac{C_P}{T} dT$$

$$S(T^*) - S(0) = \int_0^{T^*} \frac{C_P}{T} dT$$

Now, we chose to define entropies as 0 at $T = 0$ (because all molecules are stationary, there is only 1 way to arrange molecules). Furthermore, each **phase change** causes a “jump” in the graph [at the precise temperature, the heat capacity tends to infinity] and has an associated change in entropy. Taking these into account, we have

$$S(T^*) = \int_0^{T^*} \frac{C_P}{T} dT + \sum_{\text{phase changes}} \frac{\Delta H_{\text{phase change}}}{T_{\text{phase change}}}$$

- Converting entropies from one temperature to another, using different limits to the integrals above.

Gibbs Energy

- We define the **Gibbs Energy** as

$$\boxed{G = H - TS}$$

This allows us to encapsulate changes in the system *and* the surroundings simultaneously, because at **constant pressure** and **constant temperature**, we have that $\Delta G = -T\Delta S_{total}$. In such a case

- In a **spontaneous process**, G falls – ie: $\Delta G < 0$.
- At **equilibrium**, G reaches a **minimum** – ie: $\Delta G = 0$.
- It turns out that G is also the **maximum amount of non-expansion work** that can be extracted from a process at **constant pressure**.
- The first of the **Master Equations** can be derived by combining the first and second laws:

$$dU = q + w$$

$$dU \stackrel{\text{work done}}{\equiv} q - p dV$$

$$dU \stackrel{\text{reversible processes}}{\equiv} T dS - p dV$$

$$\boxed{dU = T dS - p dV}$$

And since U is a state function, this applies to all processes, not just reversible ones.

- The *second* master equation is:

$$dH = dU + p dV + V dp$$

First master
equation

$$dH \stackrel{\text{First master equation}}{\equiv} T dS - p dV + p dV + V dp$$

$$\boxed{dH = T dS + V dp}$$

- The *third* master equation is:

$$dG = dH - T dS - S dT$$

Second master
equation

$$dG \stackrel{\text{Second master equation}}{\equiv} T dS + V dp - T dS - S dT$$

$$\boxed{dG = V dp - S dT}$$

- We can use the third master equation to see how G varies with p and V at constant T :

Constant
temperature

$$dG = V dp - S dT \stackrel{\text{Constant temperature}}{\equiv} V dp$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V = \frac{nRT}{p}$$

$$\boxed{G_m(p) = G_m^o + RT \ln \frac{p}{p^o}}$$

Where G_m are standard molar Gibbs energies and p^o is a standard pressure. Note that this predicts that the decrease in pressure is spontaneous.

- And the variation of G with T are constant pressure:

Constant
pressure

$$dG = V dp - S dT \stackrel{\text{Constant pressure}}{\equiv} -S dT$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

S , however, varies with temperature, and so we can't integrate this easily. However, we note that

$$\frac{d}{dT}(GT^{-1}) = \frac{1}{T} \frac{dG}{dT} - \frac{G}{T^2} \stackrel{\text{From above}}{\equiv} -\frac{S}{T} - \frac{G}{T^2} \stackrel{\text{Definition of } G}{\equiv} -\frac{S}{T} - \frac{H - TS}{T^2} = -\frac{S}{T} - \frac{H}{T^2} + \frac{S}{T}$$

$$\boxed{\frac{d}{dT}\left(\frac{G}{T}\right) = -\frac{H}{T^2}} \quad (\text{constant pressure})$$

This is the **Gibbs-Helmholtz Equation**.

Chemical Changes

- Δ_r denotes the change that occurs when **one mole of reaction** takes place at a specified composition.

- The **standard state of a substance is the pure form at a pressure of 1 bar and at the specified temperature**, and is denoted by a *superscript o*.
 - Note that there is no default temperature.
 - Note that Δ_r values assume *standard states*, and therefore do not take into account that in real reactions, things are slightly mixed.
- The **reference state of an element is the most stable state of that element at a pressure of 1 bar**.
- The **standard enthalpy of formation (or Gibbs energy of formation)** is the **standard enthalpy change (or Gibbs energy change)** for a reaction in which **one mole of the compound** is formed from its **constituent elements** in their **reference states**.
- Therefore, $\Delta_r H^\circ$ and $\Delta_r G^\circ$ are 0 for elements in their reference states (eg: N₂).
- For a given reaction, $\Delta_r C_p$ is, as usual, worked out by *Products – Reactants*.

Mixtures

- The **partial pressure** of a mixture of gases is the **pressure that it would exert if it occupied the whole volume on its own**. For a mixture of **ideal gases**, the partial pressure of *i*, p_i is given by

$$p_i = x_i p_{tot}$$

Where p_{tot} is the total pressure, and x_i is the **mole fraction**, given by

$$x_i = \frac{n_i}{n_{tot}}$$

- The **Gibbs Energy** of a mixture can be computed from the **chemical potentials** of each substance as follows:

$$G = n_A \mu_A + n_B \mu_B + \dots$$

In the most general case, each of these chemical potentials will depend not only on the concentration/partial pressure of the substance, but also on the composition of the *entire mixture*.

- For an **ideal gas**, the chemical potential is identical to the molar Gibbs energy at the relevant pressure – ie (from above):

$$\mu_i(p_i) = \mu_i^\circ + RT \ln \frac{p_i}{p^\circ}$$

This is because since ideal gases do not interact, then a gas at a pressure p by itself is the same as a gas at partial pressure p in a mixture.

- For **ideal solutions** (if *i* is a solute)

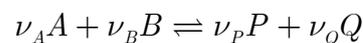
$$\mu_i(c_i) = \mu_i^\circ + RT \ln \frac{c_i}{c^\circ}$$

Where μ_i° is the standard chemical potential of the solution – ie, when the concentration is $c^\circ = 1 \text{ mol dm}^{-3}$.

- **Solids** and **pure liquids** are always present in their standard state, so their chemical potential are simply equal to their standard chemical potential.
- These considerations allow us to understand why gases mix and why reactions go to equilibrium.

Equilibrium

- The **equilibrium constant** is given by “**products over reactants**”. Notes:
 - The equilibrium constant is constant for a given reaction at a given temperature.
 - When involving **pressures**, it is denoted K_p . When involving concentrations, it is denoted K_c .
 - We need a way to ensure that it is **dimensionless** – to do that, we divide each concentration or pressure in the expression by the standard concentration or pressure.
 - Solids and liquids **do not** appear in the equilibrium constant.
- Considering the generalized reaction



The potential of each of these species is:

$$\mu_A = \mu_A^\circ + RT \ln \frac{p_A}{p^\circ}$$

$$\mu_B = \mu_B^\circ + RT \ln \frac{p_B}{p^\circ}$$

$$\mu_P = \mu_P^\circ + RT \ln \frac{p_P}{p^\circ}$$

$$\mu_Q = \mu_Q^\circ + RT \ln \frac{p_Q}{p^\circ}$$

Now, let's assume one mole of the reaction happens – then we've *gained* one mole on the right hand side, and *lost* one mole of the left hand side. So:

$$\Delta_r G = \nu_P \mu_P + \nu_Q \mu_Q - \nu_A \mu_A - \nu_B \mu_B$$

$$\Delta_r G = \nu_P \left[\mu_P^\circ + RT \ln \frac{p_P}{p^\circ} \right] + \nu_Q \left[\mu_Q^\circ + RT \ln \frac{p_Q}{p^\circ} \right] - \nu_A \left[\mu_A^\circ + RT \ln \frac{p_A}{p^\circ} \right] - \nu_B \left[\mu_B^\circ + RT \ln \frac{p_B}{p^\circ} \right]$$

$$\Delta_r G = \left[\nu_P \mu_P^\circ + \nu_Q \mu_Q^\circ - \nu_A \mu_A^\circ - \nu_B \mu_B^\circ \right] + RT \left[\nu_P \ln \frac{p_P}{p^\circ} + \nu_Q \ln \frac{p_Q}{p^\circ} - \nu_A \ln \frac{p_A}{p^\circ} - \nu_B \ln \frac{p_B}{p^\circ} \right]$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln K$$

However, at equilibrium, $\Delta_r G = 0$. Therefore:

$$\Delta_r G^\circ = -RT \ln K$$

- Activities of solids and pure liquids do not appear in the equilibrium constants because they do not change. However, they *do* affect $\Delta_r G^\circ$, and therefore the position of the equilibrium.
- In general:
 - If $\Delta_r G^\circ > 0$, reagents are favoured.
 - If $\Delta_r G^\circ < 0$, products are favoured.
 - In general, if $|\Delta_r G^\circ| > 40 \text{ kJ mol}^{-1}$, then the reaction either doesn't happen at all, or goes to completion.
- Le Chatelier's Principle:
 - Removing one reagent shifts our horizontal position of the *Conc/G* curve in one direction – as a result, it'll try and shift itself back towards equilibrium, and re-generate that reagent.
 - Changing temperature – K is clearly temperature dependent, not only because of the T term in $\Delta_r G^\circ = -RT \ln K$, but also because of the dependence of $\Delta_r G^\circ$ itself on temperature. See below.
 - Since we know that $\Delta_r G^\circ = -RT \ln K$ and that $\Delta_r G^\circ$ doesn't change at a given temperature, it follows that K does not change with pressure. However, the composition *does* change [to “keep K constant”]. The best way to deal with such things is to define a **dissociation constant** and to work out an expression for K in terms of that dissociation constant. This can then be re-arranged to find the dissociation constant in terms of the total pressure.
- Changing temperature – two approaches:
 - The Quick Approach
 - Substitute the expression for $\Delta_r G^\circ$ into the equilibrium equation:

$$\Delta_r H^\circ - T \Delta_r S^\circ = -RT \ln K$$

$$\ln K = -\frac{\Delta_r H^\circ}{R} \frac{1}{T} + \frac{\Delta_r S^\circ}{R}$$
 This tells us that the reaction of K to heat depends on whether the reaction is exothermic or endothermic.
 - It also gives us an indirect way for finding $\Delta_r H^\circ$ and $\Delta_r S^\circ$, using a plot of $\ln K$ against $1/T$.
 - Of course, all these assume that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ do not vary with temperature.
 - The van't Hoff Isochore
 - Substitute the expression for $\Delta_r G^\circ$ into the Gibbs-Helmholtz Equation:

$$\frac{d}{dT}(-R \ln K) = -\frac{\Delta_r H^\circ}{T^2}$$

$$\boxed{\frac{d \ln K}{dT} = \frac{\Delta_r H^\circ}{RT^2}}$$

This is the *van't Hoff Isochore*.

- Integrating between two temperatures:

$$\ln K(T_2) - \ln K(T_1) = -\frac{\Delta_r H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

Electrochemistry

- Chemical reactions involving reductions and oxidations can be thought of as involving the transfer of electrons.
- If the reaction is set up in an electrochemical cell, we can arrange for the electron transfer to take place through an external circuit. This allows us to convert chemical energy (in fact, Gibbs energy) into electrical energy.
- **Conventions**
 - Each half-cell reaction is written as a **reduction** – the electrons are on the **LHS** of the reaction.
 - The **conventional cell reaction** is found by taking (*RHS half-cell reaction*) – (*LHS half-cell reaction*).
 - The **cell potential** is that of the **RHS measured relative to the LHS**.
 - The **shorthand** used to write cells involves
 - A **vertical line**, |, used to **separate different phases**.
 - A **comma** use to **separate same phases**.
 - The **junction between the two solutions** marked as ||.
 - The aqueous species nearest the junction, **most oxidized species nearest the junction**.
 - Any inert metal conductor is always outmost.
- At **constant temperature and pressure**, the following holds, where E is the EMF of the cell with conventional cell reaction with change in Gibbs energy $\Delta_r G_{cell}$, involving the transfer of n electrons.

$$\boxed{\Delta_r G_{cell} = -nFE}$$

Since we know that $(\partial G / \partial T)_p = -S$, we also have that

$$\Delta_r S_{cell} = nF \left(\frac{\partial E}{\partial T} \right)_p$$

In practice, all we need to do is plot a graph!

- In real solutions, the chemical potential has to be expressed in terms of the **activity**:

$$\mu_i(a_i) = \mu_i^o + RT \ln a_i$$

Where a_i is a dimensionless quantity and

$$a_i \rightarrow \frac{c_i}{c^o} \quad \text{as} \quad c_i \rightarrow 0$$

For ions in solution, *Debye-Huckel theory* gives a reasonable estimate of activities in terms of concentration.

- The **Nernst Equation** is

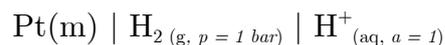
$$E = E^o - \frac{RT}{nF} \ln \frac{(a_p)^{\nu_p} (a_q)^{\nu_q}}{(a_a)^{\nu_a} (a_b)^{\nu_b}}$$

In an ideal gas, activities must be replaced by p_i/p^o . Note that the fraction on the right hand side is *not* necessarily an equilibrium constant (even though it has the same form – products over reactants) because the activities might not be those at equilibrium.

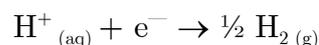
- We can also use this equation to express half-cell potentials, and it turns out that

$$E_{cell} = E_{1/2}(\text{RHS}) - E_{1/2}(\text{LHS})$$

- However, it is impossible to calculate $\frac{1}{2}$ -cell potentials in isolation, so we choose a **reference**, with respect to which all $\frac{1}{2}$ -cell potentials are quoted. These are called **standard half-cell potentials**, and are calculated against the **standard hydrogen electrode** – H_2 gas at *1 bar* in contact with an aqueous solution of H^+ of *unit activity*. An *inert Pt electrode* is used to make electrical contact:



The half-cell reaction is



The standard-half-cell potential is calculated using this electrode on the *left*. E is affected by temperature (rather obvious given its relation to ΔG) and so must be tabulated at a certain temperature.

- We can determine whether the conventional cell reaction will take place by remembering that $\Delta_r G_{cell} = -nFE$:
 - If E is positive, the conventional cell reaction is spontaneous.
 - If E is negative, it's not!

Since potentials are affected by concentrations of species involved, simply altering the concentration can alter the spontaneous cell reaction.

- This can also be used to assess **redox stability**. If we have two compounds A_o and B_o , we consider the two half cells:



And we note that:

- If $E_A > E_B$, the first reaction has a greater driving force than the second, and A_O will oxidize B_R . [Or we can say that the reverse of the second reaction has a greater driving force than the reverse of the first, so B_R will reduce A_O].
- And vice-versa.

Again, it is important to remember that there is still a concentration dependence, even though it is only a logarithmic one...

- These ideas can also be used in other ways:
 - **To find solubilities.** If we want to find the solubility of MX , we find cells that add or subtract to give $MX \rightarrow M^+ + X^-$, and bingo!
 - **To find thermodynamic parameters of ions.** For ions **in solution**, we define that

$$\Delta_f H^\circ(H^+) = \Delta_f G^\circ(H^+) = 0$$

We can then consider a cell reaction involving the standard hydrogen electrode on the LHS and an electrode involving an ion of interest on the RHS. An expression can be found for the $\Delta_r G^\circ$ of the resulting reaction [which will simply be the $\Delta_r G^\circ$ of the ion of interest] and equated to the E of this cell.