# School of Physics and Astronomy

# Junior Honours **Thermodynamics** GJA 2019-2020

## Lecture TOPIC 18 Application of chemical Potential and Self assembly

### Entropy of Mixing - Ideal solution

Consider a multicomponent solution at fixed temperature, where each component obeys Raoult's Law, and there are no interactions.

The chemical potential of each component is then

$$\mu(T, p_i) = g(T, p_i) = g_0 + RT \ln p_i/P_0$$

Where we have to define some reference state $g_0$ as the "zero" of free energy, and can't pick $T = 0$ because the ideal gas entropy is infinite there. A convenient choice here is that $P_0$ is the total pressure, so that $p_i/P_0 = x_i$, the fraction of species $i$ in the mix.

The specific entropy of each component in the mixture is then

$$s = -\left(\frac{\partial g}{\partial T}\right)_P = -R \ln x_i$$

From which the total entropy of the system is

$$S = -\sum x_i s_i = -\sum x_i R \ln x_i$$

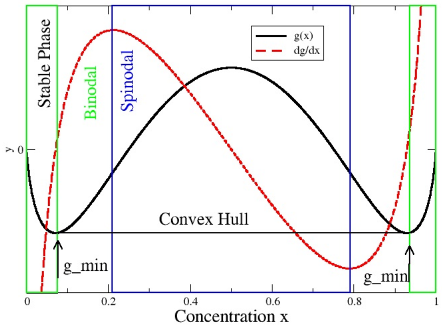
Although derived from the non-interacting approximation, this expression is reasonably accurate for interacting case.

### Two component solution

For "Solubility" in TOPIC 17, we considered a open system in contact with a large "surroundings". We can do similar analysis for a two component system at fixed P,T, which, from Gibbs Phase Rule, may have two phases.

Consider two immiscible substances, A and B, which repel one another. The enthalpy associated with this repulsion can be written as

$$H = H_0 x_A x_B$$



$x_A x_B$ is an approximation for how many A-B interactions there are. In principle there would be AA and BB interactions, but for fixed amounts of A and B, we can take those into the reference energy. If the AA and BB interactions were different from each other, $g(x)$ would be asymmetric and the algebra more tedious, but the general principles are the same.

Note that $H$ involves both types of atom. We can't determine the chemical potential of A ($\mu_A$) without knowing the concentration of B. Nevertheless, we can write the *total* Gibbs free energy for the whole system:

$$G = H_0 x_A x_B + x_A RT \ln x_A + x_b RT \ln x_B$$

In a two component system, the fractions of A nd B must add up to 1, so $x_B = 1 - x_A$.

$$G = H_0 x_A(1-x_A) + x_A RT \ln x_A + (1-x_A)RT\ln(1-x_A)$$

The system seeks to minimize its free energy, so we have

$$\left(\frac{dG}{dx_A}\right)_T = \frac{H_0}{RT}(1-2x_A) + \ln\frac{x_A}{1-x_A} = 0$$

This transcendental equation can be solved numerically or with a computer algebra package like Wolfram Alpha. Trivially, both terms in this expression are zero $x_A = 0.5$, but for large $H_0$ this is a maximum rather than a minimum. In that case, there are two other solutions at large and small $x_A$, each corresponding to minima in G. An approximate solution comes from assuming that $x_A << 1$. In that limit we recover $x_A \approx \exp(-H_0/RT)$.

For a closed system, the composition of the system is fixed, so varying the total $x_A$ isn't possible. Even in those cases, if $x_A = 0.5$ *maximises* the free energy, then the system can spontaneously break into a two-component mixture where each component has different $x$. This is similar to how the two-phase van der Waals fluid with fixed volume minimises its Helmholtz free energy (TOPIC 13).

### Binodal and Spinodal Decompostion

Figure shows $g(x)$ and its derivative with $\frac{H_0}{RT} = 3$. For higher temperatures, $g(x)$ has a single minimum.

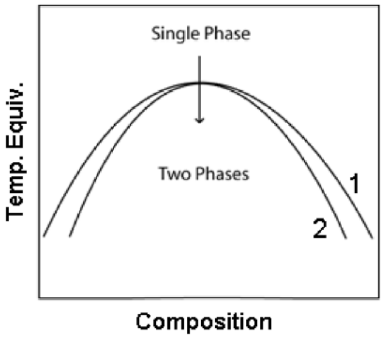
Suppose the total fraction $x_A$ of the system is fixed at some value away from 0.5. The material minimises its Gibbs Free Energy along the convex hull (see figure). At large and small $x$, this is a single phase. At intermediate concentration the system can lower G by breaking into two phases with $x_{low}, x_{high} = x(g_{min})$, the *solubility limits*. the relative amounts of high and low concentration is determined by the constraint on the total $x_A$, leading to the *lever rule*

$$c_{low}x_{low} + (1-c_{low})x_{high} = x_A$$

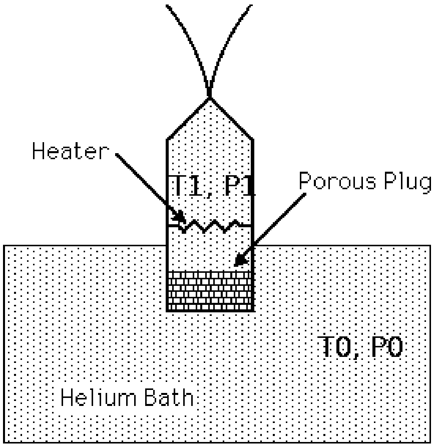
Now consider the second derivative, $\frac{d^2g}{dx^2}$, on the single phase. If this is negative, a small fluctuation into slightly high/slightly lower concentration will lower $G$: (the maths is identical to proving heat capacity $\frac{d^2g}{dT^2}$ must be positive). Such a single phase mixture, which could have been prepared by stirring or rapid cooling from high temperature, is out of equilibrium and will spontaneous split into two components, so-called *spinodal decomposition.*

In the region of concentration just beyond the solubility limits, the second derivative is positive, and the material is stable against small fluctuations. It can still lower its Gibbs Free Energy by decomposing into two phases, but because there is no simple way to do so, this process, *binodal decomposition*, happens slowly and the single phase may exist metastably.

The solubility limits increase with temperature, so binodal (1) and spinodal (2) regions can be delineated on a temperature-concentration phase diagram as shown.



## Superfluid Helium Fountain effect



Below 2.17K, superfluid helium II is a liquid which consists of two components: a normal fluid, and a superfluid of atoms in the same quantum state with zero viscosity and zero entropy.

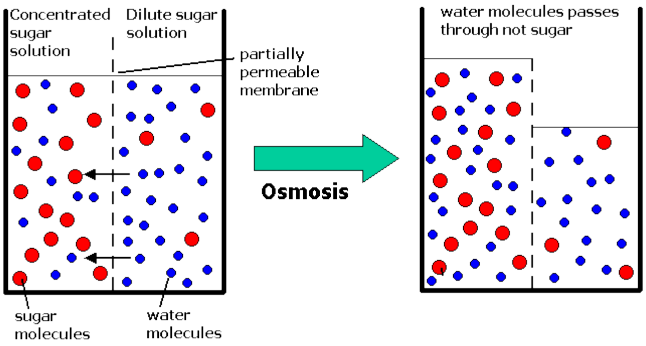
Consider two vessels, ("reservoir", and "system") connected by a plug through which only the superfluid component can flow[1]. Since the superfluid components are in contact, He II must have the same $\mu$ in both reservoir, and system. i.e. $\Delta\mu = 0 = v\Delta P - s\Delta T$, where $\Delta$ is the difference between reservoir, and system.

If the *system* is then heated, to keep the chemical potentials equal there will be a pressure difference between system and reservoir $\Delta P/\Delta T = s/v > 0$. This high pressure in the system is sufficient to generate a fountain of helium II, forever spraying into the air and falling back to the reservoir.

The superfluid "quantum ground state" extends through a large region of space, including liquid in each vessel, and the fountain itself. The second law isn't violated because heat is being supplied - it's just a fancy heat engine.

The "ammonia fountain" looks similar, but is a more prosaic example of reduction in chemical potential overcoming gravitational potential. Ammonia in water has a very low chemical potential, so water can be sucked up a tube against gravity into an ammonia atmosphere, with inertia producing the fountain. However, once equilibrium is reached, the fountain stops.

## Osmosis



Osmosis exploits the fact that particles flow down gradients of chemical potential, not concentration. High concentration *usually* means high chemical potential. But not always.

Some biological systems have a special type of *semipermeable membrane* which allows heat transfer, sustains a pressure differences, but only allows some particle flow - say type w (water) but not type s (sugar).

Consider a system comprising two regions A and B separated by such a semipermeable membrane, and allowed to equilibrate. Since water can flow freely, equilibrium requires $\mu_A^w = \mu_B^w$, and partial pressure $P_A^w = P_B^w$. But the sugar particles are not able to equilibrate, $\mu_A^s \neq \mu_B^s$, and consequently total pressures in A and B differ.

The simplest case treats both particles as ideal gases with sugar particles only in region A. Now the "osmotic pressure": the pressure difference between the two regions, is simply the partial pressure $P_A^s$. If the particles interact (as real water and sugar do!) things get more complicated. If the interaction is attractive.

- The interaction lowers the pressure (like *a* in the van der Waals gas), Raoult's Law fails.

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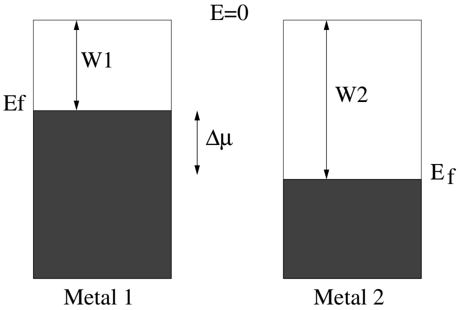
[1] The zero viscosity of the superfluid component of helium II makes such a plug possible

- The attraction lowers the chemical potential of the water, causing it to flow from the low pressure region to the high pressure region until the pressure increase raises $\mu$ to balance the attraction. So one side contains more sugar *and* more water.
- Biological cell are like this, the osmotic pressure keeping them stiff and rigid. It their membranes fail, plants wilt. If placed in a hypertonic environment (too much external solute) cells can have water sucked out of them.

### Electrons and Fermi Energy



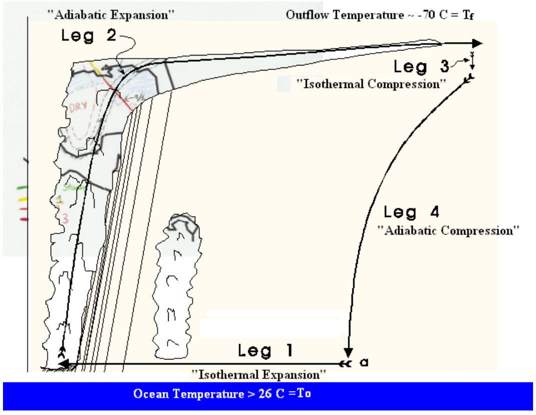
In the metal, electrons occupy energy states up to the "Fermi Level" Adding an electron to an isolated metal means putting in the lowest unoccupied energy state, thus the chemical potential for the electron is $\mu = E_F$.

Different metals have different in work functions, $W$: the energy needed to remove an electron from the Fermi level to "far away" - which gives us a reference potential $\mu^0$ appliable to both metals.

Thus $\mu_1 = \mu^0 - W_1 \neq \mu_2 = \mu^0 - W_2$. When the metals are brought into contact, the system lowers its Free Energy by flow of electrons from one metal to the other. This equates to a potential difference ("Voltage"), equal to the difference in work functions divided by electron charge $V = (\varepsilon_{W,1} - \varepsilon_{W,2})/e$. A "Pile" of such pairs forms a battery.

A *thermoelectric material* exploits the fact that $\mu$ is a function of T. A temperature gradient induces electrons to flow from one end to the other - if they flow via a wire instead of through the material then heat gradients can be used to make electricity.

### Hurricanes



A hurricane is a self assembling heat engine. The hot reservoir is the ocean surface ($T_h \approx 300K$), the cold reservoir is the top of the atmosphere, ($T_c \approx 200K$) work is done creating winds. Elements of the cycle can be idealised as a Carnot cycle:

**Isothermal expansion** - the eye, is at low pressure. Air spirals across the ocean towards it being heated and absorbing water vapour as it goes.

**Adiabatic expansion** Hot air/water vapour rises from the eye to even lower pressure at high altitude, cooling as it goes.

**Isothermal compression** Water vapour condenses, releasing latent heat. Rain falls.

**Adiabatic compression** In theory, air drops back to sea level.

The spiralling is caused by Coriolis forces. This stabilises the structure, but is not an essential part of the thermodynamics. When the hurricane comes ashore, it loses contact with its heat source and the engine stops. In the absence of land, this would take a long time (e.g. Great Red Spot on Jupiter).