School of Physics and Astronomy

Junior Honours **Thermodynamics**   GJA 2019-2020

Lecture TOPIC 17 Synopsis:Chemical Potential

Chemical potential μ - treatment of open systems

So far we have considered closed systems (fixed number of particles). Now we allow particle exchange: supposing we add dN extra particles to a single component system, without work or heat, the energy must change. So we have to modify the combined 1st and 2nd law,

$$dU = TdS - PdV + \mu dN \qquad \text{with } \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \qquad (1)$$

The above modification is mathematically equivalent to including an extra source of work. This is not especially useful, since it is unusual to be able to add particles (dN) without also changing the entropy (dS). More convenient boundary conditions require the other thermodynamic potentials. All the definitions $F = U - TS$, $H = U + PV$, $G = H - TS = F + PV$ are unchanged.

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{T,P} \qquad (2)$$

Consider changes in extensive Gibbs free energy, $dG = -SdT + VdP + \mu dN$. We can increase all the extensive quantities by a factor of α: $\Rightarrow \alpha G(P,T,N) = G(P,T,\alpha N)$. Taking the derivative of both sides with respect to α gives:

$$G = \left(\frac{\partial G(P,T,\alpha N)}{\partial \alpha}\right)_{P,T} = N\left(\frac{\partial G(P,T,\alpha N)}{\partial(\alpha N)}\right)_{P,T} = \frac{N}{\alpha}\left(\frac{\partial G(P,T,\alpha N)}{\partial N}\right)_{P,T} = N\left(\frac{\partial G(P,T,N)}{\partial N}\right)_{P,T}$$

$$\boxed{G = N\mu \quad \text{for a single component system, } \mu \text{ is the specific Gibbs free energy}} \qquad (3)$$

$$\boxed{s = -(\partial \mu/\partial T)_p, \qquad v = (\partial \mu/\partial p)_T; \qquad \text{for a single component system}} \qquad (4)$$

Once again, Gibbs is special because its natural variables, T and P, are *intensive*. The Gibbs free energy tells us how much work is done in adding a particle to a system.

Equilibration of two regions exchanging particles

Imagine dividing an isolated closed system into two parts, A and B, separated by a freely moving permeable membrane. Since it is isolated, total U, N and V are conserved, so for exchanges of energy, particles or volume we have:

$$dU_A + dU_B = 0, \qquad dN_A + dN_B = 0, \qquad dV_A + dV_B = 0.$$

And $dS_A + dS_B \geqslant 0$ with equality at equilibrium.

Rearranging EQN 1 we find: $dS = \frac{dU}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN$, which, when applied to the two-part isolated system gives

$$\left(\frac{1}{T_A} - \frac{1}{T_B}\right)dU_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right)dV_A - \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\right)dN_A \geqslant 0$$

So at equilibrium, T, P **and chemical potential** are equal $\mu_A = \mu_B$. The first term shows that energy flows from hot to cold until $T_A = T_B$. The second term shows that a higher pressure region will increase its volume (for equal T) and the third that particles flow from high to low chemical potential (for equal T). **Particles (mass) flow along gradients of the chemical potential**.

Mass flow can be used to do work. The Availability (maximum work extractable), when a reservoir can exchange particles with a system, becomes:

$$A = U - T_0 S + p_0 V - \mu_0 N \tag{5}$$

$$\Rightarrow dA = (T - T_0)\, dS - (p - p_0)\, dV + (\mu - \mu_0)\, dN \leq 0 \tag{6}$$

So a chemical battery or an explosive is able to do work because its chemical potential is out of equilibrium with its environment.

Equilibrium in Multicomponent system

We now revisit the Gibbs Phase Rule. Recalling the Second Law: a system is in equilibrium when its *total* Gibbs free energy is minimised. For a multicomponent system, open boundary conditions we must specify μ_i for each component.

An N-component open system requires *2+N* boundary conditions, e.g. P,T and μ for each component.

This is very challenging when the components interact. We start by looking at some special cases.

Chemical potential of ideal gases

Ideal gases describe the limit of any dilute amount of weakly interacting material. This includes gases, but also reagents in solution, conduction electrons in solid, photons in cavities, dark matter etc. Because there are no interactions, we can minimise the *total* Gibbs free energy of an ideal gas mixture by minimising the components independently.

For a pure ideal gas, consider the intensive quantity $g = h - Ts$. Recalling that for an ideal gas $h = u + Pv = u(T) + RT$ is a function of temperature only, and the ideal gas entropy is $s = c_P \ln(T/T_0) - R \ln(P/P_0) + s_0$ and integrating

$$\mu - \mu_0 = c_P(T - T_0) + RT \ln(P/P_0) - c_P T \ln(T/T_0)$$

Note that we need to define a reference temperature and pressure. It would be highly inconvenient to set to P=0, T=0, because the ideal gas doesn't obey the Third Law.

The chemical potential *increases* as the pressure in the gas increases isothermally. This means more work is required to add a particle to a gas at high pressure or, equivalently, less work is required to supply a particle from a region of high chemical potential. In an open system, it is useful to specify the chemical potential of the surroundings as a boundary condition.

n.b. using the ideal gas law the chemical potential becomes

$$\mu - \mu_0 = c_P(T - T_0) + RT \ln(V_0/V) - c_v T \ln(T/T_0)$$

at fixed T, this can obviously be lowered by maximising V, i.e. the gas will occupy the entire volume available.

Chemical potential of interacting particles

Consider a system containing two types of interacting particles, the internal energy of one subsystem of particles u_A now depends on the concentration of the other. This means that to minimise G, we can no longer simply minimise all the g_i independently. This generates some transcendental equations, so we'll return to this in the next topic.

Raoult's Law and Dalton's Law for Ideal Gases

Non-interacting atoms in the same system can be treated as *independent* ideal gases. Their temperature and volume are the same, chemical potential depends on the *partial* pressure. Higher concentration of a gas means higher chemical potential.

> Raoult: The partial pressure of the solute is proportional to its concentration $p_i V = N_i RT$.

> Dalton: The total pressure is the sum of the "partial pressures" of each component ($P = \sum_i p_i$).

Taken together, these extend the applicability of the ideal gas to any non-interacting component: dilute chemicals in solution, photons in a cavity etc.

In a closed system, it follows

External contributions to system's internal energy - gravity and planets

Additional terms might be added to the potential energy, e.g. *mgz* in a gravitational field ($z =$ height; m=molar mass). This term will appear in the chemical potential:

$$\mu = u + Pv - Ts + mgz$$

For an ideal gas, we can consider each component independently. So the *mgz* term means that heavier gases will sink.

Chemical potential determines the structure of a planetary atmosphere. At equilibrium, μ must have the same value at all altitudes. Since the external gravitational field $g(z)$ varies with height, the pressure is *not* constant.

Example: Solubility of gas x in water

Consider a component in an open system with external boundary conditions T_0, P_0 and chemical potential, $\mu_x^{(0)}$, set e.g. by the partial pressure of gas x above some water. Suppose that the specific enthalpy of solution (binding of the x atom to the solvent) is δh_x per mole of particles dissolved. What is the concentration, c_x, of x particles in the system at equilibrium?

The chemical potentials of system and surroundings must be equal. So, assuming ideal gas entropy ($T_x = T_0$) and Raoult's Law for partial pressure in solution ($p_x = P_0 N_x / N = c_x P_0$):

$$\mu_x^{(0)} = \mu_x = \delta h + RT_0 \ln p_x / P_0$$

and rearranging we find:

$$c_x = \exp(\mu_x^{(0)} - \delta h) / RT_0$$

So, even if $\delta h \gg \mu_x^{(0)}$ (x is "insoluble"), there is still some x in solution, and the amount increases with temperature. For $\delta h < \mu_x^{(0)}$ (x is "soluble") the concentration is larger than 1, which indicates that the ideal gas (dilute solution) approximation has broken down.

Thermodynamics in Chemistry

In many situations there are many different particle species, e.g. in chemistry molecules react to form other molecules; a chemical potential can be defined for each one in terms of its partial pressure. The Central Equation and definition of G can be extended straightforwardly giving:

$$dG = -SdT + VdP + \sum_i \mu_i dN_i \qquad \text{and } G = \sum_i \mu_i N_i \qquad (7)$$

the derivative of the second expression is $dG = \sum_i \mu_i dN_i + N_i d\mu_i$, and equating these two expressions for dG yields the **Gibbs-Duhem relation**:

$$\boxed{S\,dT - V\,dP + \sum_i N_i\,d\mu_i = 0} \qquad (8)$$

For a typical case of a chemical reaction with P and T fixed by the boundary conditions, the equilibrium is at $\sum_i N_i d\mu_i = 0$.

For a closed system (ie no particle exchange) in equilibrium with a T, P reservoir G is minimised at equilibrium. If chemical reactions are possible, then $dN_i \neq 0$ and reactions occur spontaneously until G is minimised. From EQNs 7 & 8,

$$\sum_i \mu_i dN_i = 0 \qquad \text{closed system at equilibrium, T and P fixed by boundary condition.} \qquad (9)$$

Both $dG = 0$ and $dF = 0$ give the same result so this holds for fixed T and V boundaries also. There will be some constraints on dN_i because while molecules can react, the number of atoms of each element is fixed.

Example (further examples given online)

Consider a chemical reaction in a closed system, e.g. $2H_2 + O_2 \leftrightarrow 2H_2O$. Molecules can react, but the number of atoms of each element is fixed:

Conserving the number of atoms can be represented mathematically with a constraint

$$\sum_i b_i dN_i = 0$$

where the sum runs over components H_2, O_2 and water with $b_H = 2$, $b_O = 1$, $b_W = -2$.

We use this constraint to eliminate the dN_i in the equilibrium condition EQ. 9

$$\sum_i b_i \mu_i = 2\mu_H + \mu_O - 2\mu_W = 0 \qquad (10)$$

This defines the chemical equilibrium of a reaction in terms of the chemical potentials of the reagents. Actually calculating the value of μ_i is complicated, since it involves the strength of the bonds in the molecules. An approximation would be to treat each component as an ideal gas, and add a constant "chemical bonding" internal energy u_i to each species, with $2u_H + u_O > 2u_W$ indicating that the reaction is exothermic.

However we can see some general principles. At high T, entropy will dominate and the equilibrium will favour $2H_2 + O_2$. If we add more of one of the reagents, say H, then its partial pressure and μ_H will increase. But that would mean the equation 10 is no longer satisfied. To return to equilibrium (i.e. to minimise G), the system reacts to create more water (increasing μ_W, reducing μ_H and μ_O).

Following a similar argument for two phases of the same substance, (e.g. gas+liquid) gives $b_1 = -b_2$ so the equivalent of equation 10 requires the chemical potentials to be equal, as we have seen. For multiple components this is not the case.

Reaction between "ideal gases" (PV=NRT) at fixed T,N (Omitted 2019)

The Gibbs free energy is a property of the whole system, but we can define separate chemical potentials for each component, to describe how a reaction reaches equilibrium, so:

$$dG = V \sum_i dp_i - SdT + \sum \mu_i dN_i$$

and for a system of ideal gases (labelled i) with fixed $T = T_0$, $N = \sum N_i$):

$$dG \equiv \sum_i d\mu_i = \sum_i \frac{RT}{p_i} dp_i$$

Substituting these expressions for μ_i into the formula for the reaction constraint

$$\sum_i b_i(\mu_i^0 + RT \ln[p_i/p_i^0]) = 0 \tag{11}$$

with μ_i^0 the chemical potentials at reference pressure p^0. p_i are the partial pressures for each species. The sum can be converted to a product inside the logarithm.

$$\ln(K) \equiv \ln\left[\prod_i (p_i/p_0)^{b_i}\right] = -\frac{\sum_i b_i \mu_i^0}{RT} \quad\Longrightarrow\quad K(T) \equiv \prod_i (p_i/p_0)^{b_i} = e^{-\frac{\sum_i b_i \mu_i^0}{RT}} \tag{12}$$

Defining the *equilibrium constant $K(T)$* which gives the proportions of reactants in equilibrium. Differentiation gives a relation between $K(T)$ and the Enthalpy of reaction:

$$\left(\frac{\partial(\ln K)}{\partial T}\right)_p = \frac{1}{RT^2} \sum b_i(\mu_i^0 + T s_i^0) = \frac{\sum b_i H_i^0}{RT^2} \tag{13}$$

Recalling that b_i are just constants to balance the reaction equation, this can be written $d\ln(K)/dT = \Delta H/RT^2$ where ΔH is the molar heat of reaction. The equation is known as "van Hof't isobar" equation in chemical thermodynamics. ΔH is experimentally measurable as the heat of reaction in a continuous flow process.

Notice the similarity between the equilibrium constant $K(T)$ and the Boltzmann Factor for the probability of observing a microstate: $\exp(-\Delta E/k_b T)$. Using the free energy accounts for the entropic contribution in the macrostate.

Nonequilibrium systems

The ideal gas Chemical Potential depends only on P and T, but for interacting particles those interactions contribute to the internal energy u, and hence to $g = u + Pv - Ts$. If the interactions are between different species, say i and j, then g_i depends on the concentration of the other species j. Concentration gradients of j then cause the flow of i-type molecules. Combined with a membrane which only allows some species to pass through, this allows inhomogeneous local regions to maintain themselves. Ultimately, such regions can be called "life".