

## Review: Some important points

Here is a brief list of things you should be familiar with when taking the final....

- State Function: They are path independent (Energy, Entropy, Enthalpy, Gibbs, Helmholtz):

$$\Delta U = \int \bar{d}q + \int \bar{d}w \quad (1)$$

$U$  is a perfect differential,  $q$  and  $w$  are usually not. Unless one of them is zero.

- Intensive Variables: Size Independent
- Extensive Variables: Size Dependent
- You should be able to identify the type of system: Isolated, Closed, Open, Adiabatic
- Zeroth Law: Described how a thermometer works: A Thermometer is a system that changes its properties as a function of temperature in a predictable way. When another system is in **thermal equilibrium** with it, we know the temperature of such system.
- Types of Processes: Adiabatic, isobaric, isochoric, isothermal
- There are several ways we can do work on a system: compression, polarization, magnetization, etc.
- First Law:  $\Delta U_{isolated\ system} = 0$ .  
Since energy is a conserved quantity, it is also a perfect differential and  $\oint U = 0$
- Ideal Gas:  $PV = nRT$   
Internal Energy of an Ideal Gas:  $\Delta \bar{U} = \int_0^T \bar{C}_V dT$ . Note that since the internal energy is a state function, this expression is valid, no matter what the process is.  
Enthalpy of an Ideal Gas:  $\Delta \bar{H} = \int_0^T \bar{C}_P dT$   
Entropy of an ideal Gas:  $d\bar{S} = \frac{\bar{C}_V dT}{T} + \frac{R}{\bar{V}} d\bar{V}$   
For an ideal gas,  $\bar{C}_P - \bar{C}_V = R$
- How to calculate a change in entropy for an irreversible system: Use a combination of reversible states that lead to the same final state.
- Useful state functions:
  - $H \equiv U + PV$
  - $F \equiv U - TS$
  - $G \equiv U + PV - TS$
  - You can create any state function you can think of. Think for example of a polarizable material, how to subtract the electric work? Would it be like an “electric enthalpy”?

- Second Law: There is a state function for any system called entropy. The sum of this state function for the system and its surroundings must be always equal or greater than zero:  $\Delta S_{Univ.} \geq 0$
- Phase transformation: There is always an enthalpy and entropy change associated with a phase transformation:  $\Delta G_{trans.} = \Delta H_{trans.} - T\Delta S_{trans.}$ .  
When the two phases are at equilibrium, the total change in the Gibbs free energy is zero. At this point, the transformation temperature is given by:  $T_{trans.} = \frac{\Delta H_{trans.}}{\Delta S_{trans.}}$ .
- Equilibrium condition: There are two ways of defining an equilibrium condition for any process: we can either calculate the total change in the entropy of the universe and make sure that it is zero; or we can use a state function such as Gibbs energy to define an equally valid local condition of equilibrium:
  - $\Delta S_{Univ.} = 0$
  - $\Delta G_{Sys.} = 0$
- Third Law:  $S_{pure\ system, 0\ K} = 0$ . Important: Entropy is not only a measure of the “disorder” of a system.
- Maximal, minimal principles: Define a condition for stable equilibrium:  $(\delta U)_{\delta S, \delta V=0} \geq 0$ ,  $(\delta G)_{\delta P, \delta P=0} \geq 0$ ,  $(\delta S)_{\delta U, \delta V=0} \geq 0$ . This means that internal and Gibbs energies must be a minimum with respect to any possible change in extensive variables. Entropy must be a maximum
- Chemical Potential:  $\mu_i = \frac{\partial G}{\partial n_i}$ . Equilibrium condition: For any **closed** system for which there are no restrictions with regard to mass transfer among phases, the chemical potential of the individual components must be equal in all phases. Any inequality in the chemical potentials would constitute a driving force for the flow of mass.
- Ideal Gas Mixture. When considering a mixture of ideal gases, it is possible to express the chemical potential of each individual component as:

$$\mu_i = \mu_{i, P_o}^o(T) + RT \ln\left(\frac{P_{Tot.}}{P_o}\right) + RT \ln(X_i)$$

- The first two terms correspond to the chemical potential of the pure components: The first term is the Gibbs energy of formation of the component at the reference pressure ( $P = P_o$ ), while the second term is the pressure contribution to the Gibbs energy. This means that by increasing the pressure, the chemical potential of a pure gas should increase.
- The last term corresponds to the entropy of mixing

The expression above could be further simplified:

$$\mu_i = \mu_{i, P_o}^o(T) + RT \ln\left(\frac{P_i}{P_o}\right)$$

, where  $p_i$  is the partial pressure of the component  $i$  in the gas mixture:  $X_i = \frac{p_i}{P_{Tot}}$ . This comes from the fact that we can relate the partial pressure of an ideal gas to the number of moles of the same gas:  $n_i = \frac{p_i V}{RT}$ .

Remember that an ideal gas mixture is a mixture of non-interacting particles.

- For a reaction  $aA + bB \rightleftharpoons cC + dD$ , we have a corresponding change in the Gibbs free energy:

$$\Delta G_{rxn} = cG_C^0 + dG_D^0 - aG_A^0 - bG_B^0$$

For this reaction, it is possible to obtain an equilibrium constant:

$$K_{eq} = \frac{p_C^c p_D^d}{p_A^a p_B^b} = \exp\left(\frac{-\Delta G_{rxn}}{RT}\right)$$

- Jacobians: State functions such as U, G, H, F, are perfect differentials. Therefore  $df = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x$ , and  $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$ .

This means that the order in which you take the second derivative of a perfectly differentiable function is order-independent.

Applying this rule to the expression for the Gibbs energy, we have:

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

Jacobians are just a mathematical tool useful to play around with maxwell's relations so we can find relationships between material properties, such as  $C_P$ ,  $C_V$ , etc.

$$\frac{\partial(u, v)}{\partial(x, y)} = \det \begin{pmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial v}{\partial x}\right)_y & \left(\frac{\partial v}{\partial y}\right)_x \end{pmatrix}$$

- Gibbs-Duhem Equation: Probably, the second most important equation of this course. It tells you how the intensive variables should change when a phase is at equilibrium. How to derive it?

1. Begin by writing down the equation for the differential of the Gibbs energy, from the definition  $G = \sum \mu_i n_i$ :  $dG = \sum \mu_i dn_i + \sum n_i d\mu_i$ .
2. Then write down the definition for  $dG$  from the derivation using the first law:  $dG = VdP - SdT + \sum \mu_i dn_i$
3. Subtract both expressions
4. Finally, you get:  $0 = SdT - VdP + \sum n_i d\mu_i$ . This means that if you increase  $T$ , for example, all the remaining intensive variables must change accordingly so the equality remains true.

- **Example of Melting Point Depression**

- Gibbs Phase Rule: VERY VERY VERY IMPORTANT.  $D + f = C + 2$ . You should know it by heart. It should be clear to you that the Gibbs Phase Rule tells you how many degrees of freedom you have when the number of components and phases is fixed. Take for example a single component  $P_3T$  phase diagram.

- Binary Phase Diagrams.

- You should know how to obtain the chemical potential of the components, by taking the slope to the curve representing the total chemical potential of the phase.
- You should be able to understand the common-tangent construction.
- Using the Gibbs energy curves and the common tangent construction, you should know how to extract the equilibrium concentrations corresponding to the phase boundaries and viceversa.
- Understand the limiting behavior of the gibbs energy curves and chemical potentials.
- Know how to apply the level rule:

$$f^{\alpha} = \frac{X_B^{\beta} - X}{X_B^{\beta} - X_A^{\alpha}}$$

- Phase diagrams

- Application of Phase Rule.
- Know how to apply the Lever Rule.
- Understand the concept of tie-lines.

If you understand all this concepts, you are in good shape and should be able to ace the final :-).