

- ❑ Brief review or introduction to Classical Thermodynamics...
- ❑ Hopefully you remember this equation from chemistry. The Gibbs Free Energy (G) as related to enthalpy (H) and entropy (S) and temperature (T).

$$\Delta G = \Delta H - T\Delta S$$

- ❑ We are going to expand upon this a bit.
- ❑ **Question:** Why study thermodynamics?
- ❑ **One Answer:** Thermodynamics allows us to describe changes in a *system* from an *initial state* to a *final state*.
- ❑ **Applications:** primarily *kinetics*
 - ✓ Phase equilibria
 - ✓ Defect equilibrium
 - ✓ Phase transformations
 - ✓ Heat transport
 - ✓ Mass transport
 - ✓ Growth of materials
 - ✓ Deposition of materials
 - ✓ Etching of materials
 - ✓ Many more ...

- ❑ What is our approach to study thermodynamics?
- ❑ Study a system of interest through the variables that:
 - ✓ mathematically describe the system
 - ✓ Are relatively easy to measure by experiments.
- ❑ How is the system of interest studied?
- ❑ We *perturb* the system and see what outcome results.
- ❑ One way of doing this is the following:
 - ✓ Determine potentially how a particular system depends on energy.
 - ✓ This can be done with mathematics.
 - ✓ That is, write an *equation* in terms of *energy*.
 - ✓ Then, mathematically perturb the energy of the system by changing one of the variables on which the system energy depends.
 - ✓ Examine how the equation of energy changes when a variable is changed.
- ❑ **If** this is done by keeping in mind what variables are easiest to measure during an actual experiment, then thermodynamics is a very useful tool.

□ Brief review or introduction to Classical Thermodynamics:

- ✓ Central equation of thermodynamics is the **fundamental equation of thermodynamics (FEOT)**.
- ✓ Describes change of *internal energy* of a system that is:
 - o initially in one state of *equilibrium*
 - o and is perturbed to another state of *equilibrium*.
- ✓ In its simplest form, **FEOT** is given by a change in internal energy of a system as described by the sum of the change in *heat, Q*, and *work, W*:

$$dU = \tilde{d}Q + \tilde{d}W \quad (1) \quad \text{1st Law}$$

- ✓ Heat and work differentials are *inexact* since they are path dependent (depend on past history).
- ✓ Heat differential is described mathematically as:

$$\tilde{d}Q = TdS \quad (2) \quad \text{2nd Law}$$

- ✓ Where *T* and *S* are the temp and entropy of the system.
- ✓ Similarly, the work differential is given by:

$$\tilde{d}W = -PdV_o + \mu dN + \sum YdX \quad (3)$$

- ✓ 1st term on right: hydrostatic work on system (hence, the negative sign) where *P* and *V* are the pressure & volume.

- ✓ 2nd term on right: chemical work done *by* the system (hence, the positive sign) where μ & *N* are the *chemical potential* and *number of particles* in the system.
- ✓ The last term allows for other forms of work performed on or by the system.
- ✓ The full form of the FEOT is:

$$dU = TdS - PdV_o + \mu dN + \sum YdX \quad (4)$$

- ✓ Two important points concerning the FEOT:
 - o 1st point: FEOT Variables – differentials and their pre-factors:
 - Differential Variables:
 - » Called *extensive* or *state* variables.
 - » Directly measurable quantities & describe the state of the system prior to (initial state) and following (final state) the system change.
 - » Changes in *state* variables are path independent (do not depend on past history).
 - Pre-factor variables to the differential variables:
 - » Called *intensive* or *field* variables.
 - » Measurable indirectly only, by means of the response of an extensive variable to a perturbed system.
 - Work performed on or by system = product between an *extensive* or *state* variable and an *intensive* or *field* variable.
 - This can be seen upon examination of the FEOT.

☐ Examples of Work as a product of extensive and intensive variables:

$$\sum YdX \quad (5)$$

Table 2.1: Types of thermodynamic work in differential form

| Thermodynamic Work | Work Differential (dW) | Intensive or Field Variable | Extensive or State Variable |
|---------------------|-----------------------------|--|-----------------------------|
| thermal | $T \cdot dS$ | T = temperature | S = entropy |
| hydrostatic | $P \cdot dV$ | P = pressure | V = volume |
| chemical | $\mu \cdot dN$ | μ = chemical potential | N = number of particles |
| strain – mechanical | $\sigma \cdot d\varepsilon$ | σ = stress | ε = strain |
| electrical | $E \cdot dP_o$ | E = electric field | P_o = polarization |
| magnetic | $H \cdot dM_g$ | H = magnetic field | M_g = magnetization |
| time dependent | $P_w \cdot dt$ | P_w = power | t = time |
| Momentum transfer | $ma \cdot dr$ | Mass acceleration | & r = distance |
| gravitational | $mg \cdot dr$ | mg = mass & gravitational acceleration | r = distance |

Note: The intensive and extensive variable pairs are known as *conjugate variables*. For example, T and S are conjugate variables.

☐ How does this apply to diffusion?

✓ Two important points concerning the FEOT (cont.):

o 2nd point: follows from the 1st point = *intensive* or “*field*” variable.

- The force acting on the system or particles in the system may be described by the negative gradient of a *field variable*.
- The force is given by:

$$F = -\nabla V \quad (6)$$

where V is the potential variable.

- Negative gradient of a field variable = *field potential*.
- Hence: **FORCE FIELD!**
- As shown in previous table, the *force (potential) field* may be:
 - » Thermal field
 - » Chemical potential
 - » Hydrostatic field
 - » Electrical field
 - » Magnetic field
 - » Stress field
 - » Gravitational field
- Although the *superposition principle* does NOT apply to *field/intensive* variables, it does to **FORCES**.
- Thus, *gradients* of the potential fields are additive.

o **Key Point:** Therefore, the *forces driving system change*, such as *diffusion*, are additive as well.

o This is the field of **KINETICS!**

□ Example: How to use the FEOT to obtain important thermodynamical relationships via *mathematics*.

- ✓ The chemical potential of atoms A is given by the thermodynamic relation:

$$\mu_A = \left(\frac{\partial E_A}{\partial N_A} \right)_{T,P} \quad (7)$$

where E_A is a *free energy* of the A atoms in B.

- ✓ Examples of *Free Energy, E*:
 - **Gibbs**, $G = G(T, P, N)$
 - **Helmholtz**, $F = F(T, V, N)$
 - **Enthalpy**, $H = H(S, P, N)$
 - **Omega potential** or **Grand Potential**, $\Omega = \Omega(T, V, \mu)$

Question 1: How are relationships between extensive and intensive variables, such as μ , obtained in thermodynamics?

Question 2: If we want to examine some *Free Energy* w.r.t. certain variables, how do we do so?

To answer these question, we need to know several mathematical properties of the *FEOT*.

□ Mathematical Properties of the FEOT

- ✓ FEOT is an *exact differential*:
 - Definition of an Exact differential:

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

Let: $M = \left(\frac{\partial z}{\partial x} \right)_y$ & $N = \left(\frac{\partial z}{\partial y} \right)_x$

Then: $\left(\frac{\partial M}{\partial y} \right)_x = \frac{\partial^2 z}{dx dy}$ & $\left(\frac{\partial N}{\partial x} \right)_y = \frac{\partial^2 z}{dy dx}$

- ✓ Since the order of differentiation is immaterial because dz is an exact differential, then:

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$$

- ✓ Apply this to FEOT.

□ Mathematical Properties of the FEOT

✓ FEOT:

$$dU = TdS - pdV + \mu dN \quad (1)$$

But FEOT is an exact differential.

Thus:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN \quad (2)$$

So, FEOT is: $U = U(S, V, N)$ the **Internal FREE ENERGY**

✓ **Coefficient And Maxwell Relations:**

o Using the property below of an exact differential, we can obtain relationships between extensive & intensive variables.

✓ **Coefficient Relations:**

o Compare equations (1) and (2), we see that:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \quad p = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

✓ **Maxwell Relations:** here we just derive one of three.

Using the exact differential relationship $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$:

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_{V,N} = \left(\frac{\partial^2 U}{\partial V \partial S}\right)_N \quad \& \quad -\left(\frac{\partial p}{\partial S}\right)_{V,N} = \left(\frac{\partial^2 U}{\partial S \partial V}\right)_N$$

$$\therefore \left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N}$$

□ Mathematical Properties of the FEOT

✓ Defining Free Energies using:

- o FEOT &
- o Properties of Exact Differentials:

✓ Example 1:

- o Enthalpy (Free Energy): $H = H(S, p, N)$

$$H = U + pV$$

Differentiate H :

$$dH = dU + pdV + Vdp$$

Substitute FEOT: $dU = TdS - pdV + \mu dN$

$$dH = TdS - pdV + \mu dN + pdV + Vdp$$

$$\therefore dH = TdS + Vdp + \mu dN \quad (1)$$

$$\text{Thus: } H = H(S, p, N) \quad (2)$$

Using (2), we can write the differential form of dH :

$$dH = \left(\frac{\partial H}{\partial S}\right)_{p,N} dS + \left(\frac{\partial H}{\partial p}\right)_{S,N} dp + \left(\frac{\partial H}{\partial N}\right)_{S,p} dN \quad (3)$$

Coefficient Relations: obtained by comparing (1) and (3)

$$\therefore T = \left(\frac{\partial H}{\partial S}\right)_{p,N} \quad V = \left(\frac{\partial H}{\partial p}\right)_{S,N} \quad \mu = \left(\frac{\partial H}{\partial N}\right)_{S,p}$$

□ Mathematical Properties of the FEOT

✓ Now that we derived the Coefficient relations...

$$T = \left(\frac{\partial H}{\partial S} \right)_{p,N} \quad V = \left(\frac{\partial H}{\partial p} \right)_{S,N} \quad \mu = \left(\frac{\partial H}{\partial N} \right)_{S,p}$$

✓ ...we can develop Maxwell Relations:

✓ We do so using the exact differential relation:

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y :$$

$$\left(\frac{\partial T}{\partial p} \right)_{S,N} = \frac{\partial}{\partial p} \left(\frac{\partial H}{\partial S} \right)_{p,N} = \left(\frac{\partial^2 U}{\partial p \partial S} \right)_N \quad \& \quad \left(\frac{\partial V}{\partial S} \right)_{p,N} = \left(\frac{\partial^2 U}{\partial S \partial p} \right)_N$$

$$\therefore \left(\frac{\partial T}{\partial p} \right)_{S,N} = \left(\frac{\partial V}{\partial S} \right)_{p,N}$$

✓ ...here we just derive one of three.

✓ What are the other two?

□ The chemical potential is very important to mass transport of particles such as:

- ✓ Atoms and molecules
- ✓ Electrons
- ✓ Phonons
- ✓ Etc.

□ Remember that from equation 7, the chemical potential is given by:

$$\mu_A = \left(\frac{\partial E_A}{\partial N_A} \right)_{T,P} \quad (7)$$

□ We have examined two free energies, U and H .

□ For U and H , does equation 7 hold?

□ Prove to yourself that it does.

□ The particles that we deal with in this class are electrons and holes which are Fermions which are particle with spin $\frac{1}{2}$.

□ The chemical potential is defined as the Fermi Energy level, E_f , as Temperature approaches absolute zero.

$$E_f = \mu \text{ as } T \rightarrow 0.$$

□ This is the primary thermo concept to understand for this class.

- What is thermodynamic equilibrium?
- Let's define them.
- Consider two phases in physical contact in a system.
The two phases could be:
 - ✓ Ice and water
 - ✓ α and β in a two phase region
 - ✓ Etc.
- The specific types of equilibrium that can exist for the two phases are:

$$T_{phase1} = T_{phase2} \quad \text{Thermal Equilibrium}$$

$$p_{phase1} = p_{phase2} \quad \text{Mechanical Equilibrium}$$

$$\mu_{phase1} = \mu_{phase2} \quad \text{Mechanical Equilibrium}$$

- Note that all of these variables are intrinsic variables.
- If one of these conditions do not exist, then equilibrium for that specific type will not be equal and a gradient (difference) exists.
- This will then be the driving force towards equil (equal) librium.
- The driving force for diffusion is when chemical equilibrium does not exist:

$$\mu_{phase1} \neq \mu_{phase2} \quad \text{i.e. } \Delta\mu \neq 0 \quad \text{or} \quad \nabla\mu \neq 0$$