

Lecture 4

Objectives:

1. Understand the need for auxiliary functions.
2. Be able to derive the differential functions from the Gibbsian equations.
3. Explain the chemical potential in physical terms.

1. Begin by reviewing the first and second law fundamental equation for a closed, pure system:

$$dU = TdS - PdV$$

$$dU = \delta Q + \delta W$$

Recall that dU is an exact differential:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_V ; P = -\left(\frac{\partial U}{\partial V}\right)_S$$

Note that U is a homogeneous function of first order. That is

$$U = U(S, V)$$

is a complete function (completely described by S and V) and that

$$U(mS, mV) = mU(S, V)$$

2. Auxiliary energy functions. We have some kind of feel for the internal energy. For a closed, pure component system, with no chemical reactions, the functions V , U and S form a complete basis, that is, we can describe all of thermodynamics by manipulating these three functions. Unfortunately, nature will not let us get away with just using U , S , and V . The problem is that we can't easily measure S , so it is difficult to develop an equation for $U = U(S, V)$. Suppose that we measure U as a function of say T and V . Is that good enough?

$$U = U(T, V)$$

but

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

so

$$U = U \left[\left(\frac{\partial U}{\partial S}\right)_V, V \right] = U(T, V)$$

Does this function carry the same amount of information as $U = U(S, V)$? Suppose that we need to know the value of S for some reason (e.g., we want to know if $dS > 0$). Can we find S from our function $U = U(T, V)$? Solve for

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial U(T, V)}{\partial S}\right)_V = F(U, V) \Rightarrow \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{F(U, V)} \Rightarrow S(T) - S(T_1) = \int_{T_1}^T \frac{1}{F(U, V)} dT$$

or

$$S(T) = \int \frac{1}{F(U, V)} dT + C$$

We can't find S because we only know how S changes **at constant volume**. The unknown constant of integration in the last equation is actually a function of V . Therefore we don't know how S depends on volume. In other words,

$$U = U(T, V)$$

contains less information than

$$U = U(S, V)$$

and we no longer have complete knowledge of the system.

For this reason people have introduced (at least) three auxiliary energy functions. They are **enthalpy**:

$$H \equiv U + PV$$

Helmholtz free energy:

$$A \equiv U - TS$$

and **Gibbs free energy**:

$$G \equiv U + PV - TS$$

The set of equations for U , H , A , and G are called the **Gibbsian equations**.

Here is a mnemonic to help you remember how these four energy functions are related:

$$\begin{array}{ccccc} & U & \xrightarrow{+PV} & H & \\ +TS & \uparrow & & \downarrow & -TS \\ & A & \xleftarrow{-PV} & G & \end{array}$$

Here is a mnemonic device to remember the mnemonic device: *U Have Great Articulation*. Go clockwise around, then do $+PV$ on top, $-PV$ on bottom, $+TS$ on left, $-TS$ on right. For example,

$$H = U + PV$$

Work out the derivative form of A given the derivative form of U and the relationship between A and U given above.

$$A = U - TS$$

$$dA = dU - TdS - SdT = TdS - PdV - TdS - SdT = -PdV - SdT$$

Likewise,

$$dH = TdS + VdP$$

$$dG = -SdT + VdP$$

3. Mixtures and open systems. A new function: the chemical potential.

Chemical potential, and the related functions activity, activity coefficient, fugacity and fugacity coefficient are among the more difficult functions to understand. I will attempt to rationalize (not derive) the chemical potential in physical terms.

- (a) Consider a mixture of H_2 , O_2 , and Pt in a closed, rigid container with adiabatic walls. What happens? Does the temperature change? If we consider the pressure low enough and the temperature high enough then the gases will be ideal. Does the internal energy change? Are there work and/or heat interactions? How does this conform to $dU = \delta Q + \delta W$? We need another function to describe the system.
- (b) Consider an open system and write down

$$dG = -SdT + VdP$$

Now add small amount of one of the components, but do so at constant temperature and pressure. Does the Gibbs free energy change? Yes, because G is extensive. How is this accounted for in $dG = -SdT + VdP$?

We deduce that for a mixture of C components, or an open system

$$U = U(S, V, n_1, n_2, \dots, n_C)$$

dU is still an exact differential, so

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S, n_i} dV + \sum_{i=1}^C \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_{j \neq i}} dn_i$$

Note that the subscript $n_{j \neq i}$ means that all mole fractions except i are held constant, e.g., if $C = 3$, $i = 2$, then $j = 1, 3$. The temperature and pressure definitions are still valid, i.e., $\left(\frac{\partial U}{\partial S}\right)_{V, n_i} = T$ and $\left(\frac{\partial U}{\partial V}\right)_{S, n_i} = -P$. Let us now **define** the **chemical potential** as

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_{j \neq i}}$$

Then our fundamental equation becomes

$$dU = TdS - PdV + \sum_{i=1}^C \mu_i dn_i$$

The equation can be written in terms of intensive variables:

$$dU = d(n\tilde{U}) = Td(n\tilde{S}) - Pd(n\tilde{V}) + \sum_{i=1}^C \mu_i d(x_i n)$$

where $x_i = n_i/n$. This can be re-written using the product rule as

$$n \left(d\tilde{U} - Td\tilde{S} + Pd\tilde{V} - \sum_{i=1}^C \mu_i dx_i \right) + dn \left(\tilde{U} - T\tilde{S} + P\tilde{V} - \sum_{i=1}^C \mu_i x_i \right) = 0$$

Since dn and n are independent and arbitrary, each grouping of variables must independently vanish. Hence, the integrated form of the internal energy equation is

$$\tilde{U} = T\tilde{S} - P\tilde{V} + \sum_{i=1}^C \mu_i x_i$$

or

$$U = TS - PV + \sum_{i=1}^C \mu_i n_i$$

The chemical potential plays an analogous role to temperature and pressure. A temperature gradient gives rise to the flow of heat, i.e., a temperature difference is like a potential for heat transfer. Likewise, a pressure gradient is a potential for mechanical work (no pressure differences, no PV work). A gradient or difference in chemical potential is the potential to perform chemical work, either by chemical reaction or by mutual diffusion. In other words, if all the components of a mixture have the same chemical potential no chemical reactions will take place, and no mutual diffusion will occur, because there is no driving force.

$$\Delta T = \text{potential for heat flow}$$

$$\Delta P = \text{potential for mechanical work}$$

$$\Delta \mu = \text{potential for chemical work}$$

An electrical analogue is the voltage. A voltage difference (120 V relative to ground) is the potential to do electrical work (turn a fan, light a room), but voltage and chemical potential are *intensive* so it is the amount of electricity (number of amps) and the amount of chemical (number of moles) reacted that tells you how much work is done.

4. What are the integrated and differential Gibbsian equations for multi-component, open systems?

Use the mnemonic device to derive them.

$$\begin{aligned}
 H &= \dots \\
 G &= \dots \\
 A &= \dots \\
 dH &= \dots \\
 dG &= \dots \\
 dA &= \dots
 \end{aligned}$$

5. Returning to the problem of H₂, O₂, and Pt in a closed, rigid container with adiabatic walls. Start with the integrated combined first & second law. Assume that the reaction goes to completion and that we have a stoichiometric mixture of H₂ and O₂:

$$\Delta U = T_2 S_2 - T_1 S_1 - V(P_2 - P_1) + \sum_{\substack{i=1 \\ \text{final}}}^C \mu_i n_i - \sum_{\substack{i=1 \\ \text{init.}}}^C \mu_i n_i = 0$$

Where the last equality comes from the first law. For an ideal gas we can write

$$\mu_i = \tilde{G}_i + RT \ln y_i = \tilde{H}_i - T\tilde{S}_i + RT \ln y_i$$

Also, $V(P_2 - P_1) = R(n_{\text{H}_2\text{O}}T_2 - n_i T_1)$, where $n_i = n_{\text{H}_2} + n_{\text{O}_2}$. So,

$$\begin{aligned}
 0 &= -R(n_{\text{H}_2\text{O}}T_2 - n_i T_1) + T_2 S_2 - T_1 S_1 + n_{\text{H}_2\text{O}} \left[\tilde{H}_{\text{H}_2\text{O}}(T_2) - T_2 \tilde{S}_{\text{H}_2\text{O}}(T_2, P_2) + RT_2 \ln(1) \right] \\
 &\quad - n_{\text{H}_2} \left[\tilde{H}_{\text{H}_2}(T_1) - T_1 \tilde{S}_{\text{H}_2}(T_1, P_1) + RT_1 \ln y_{\text{H}_2} \right] \\
 &\quad - n_{\text{O}_2} \left[\tilde{H}_{\text{O}_2}(T_1) - T_1 \tilde{S}_{\text{O}_2}(T_1, P_1) + RT_1 \ln y_{\text{O}_2} \right]
 \end{aligned}$$

Now we note that $S_2 = n_{\text{H}_2\text{O}} \tilde{S}_{\text{H}_2\text{O}}(T_2, P_2)$ and

$$S_1 = n_{\text{H}_2} \left[\tilde{S}_{\text{H}_2}(T_1, P_1) - R \ln y_{\text{H}_2} \right] + n_{\text{O}_2} \left[\tilde{S}_{\text{O}_2}(T_1, P_1) - R \ln y_{\text{O}_2} \right].$$

Therefore,

$$R(n_{\text{H}_2\text{O}}T_2 - n_i T_1) = H_{\text{H}_2\text{O}}(T_2) - H_{\text{H}_2} - H_{\text{O}_2}$$

Now, if $T_1 = 298$ K, $P_1 = 1$ bar, then we can write

$$H_{\text{H}_2\text{O}}(T_2) - H_{\text{H}_2} - H_{\text{O}_2} = n_{\text{H}_2\text{O}} \left[\Delta \tilde{H}_{f, \text{H}_2\text{O}}^\circ + \int_{T_1}^{T_2} \tilde{C}_{P, \text{H}_2\text{O}} dT \right]$$

Using $\Delta \tilde{H}_{f, \text{H}_2\text{O}}^\circ = -2.418 \times 10^5$ J/mol and $\tilde{C}_{P, \text{H}_2\text{O}} = 29.163 + 1.449 \times 10^{-2}T - 2.02 \times 10^{-6}T^2$ (in J/mol K). $n_{\text{H}_2\text{O}} = 1$ mol, and $n_i = 1.5$ mol, we can solve for T_2 . Matlab gives $T_2 = 6203.6$ K.