Lecture 11: 10.15.05 Models of the chemical potential

Today:

Reading: Engel and Reid 6.3, 6.4, 6.5, 9.1, 9.2, 9.5

Supplementary Reading: -

ANNOUNCEMENTS :

QUIZ 1 : RETURNED END OF CLASS TODAY
AVE: ≃ 81 ± 7

PROBLEM SET 4: WILL BE POSTED THIS EVENING
DUE 1 WEEK FROM THIS FRIDAY

Last time

CHEMICAL POTENTIAL MEASURES CHEMICAL DRIVING FORCES:

2-COMPONENT, 2-PHASE $\overset{\text{CLOSED}}{\text{SYSTEM}}$, AT CONST. T, P:

$$dG = (\mu_A^\alpha - \mu_A^\beta)dn_A^\alpha + (\mu_B^\alpha - \mu_B^\beta)dn_B^\alpha = 0$$

EQUILLIBRIUM

CHEMICAL:
$$\mu_A^\alpha = \mu_A^\beta$$
$$\mu_B^\alpha = \mu_B^\beta$$

EQUALITY of CHEMICAL POTENTIALS

EQUILIBRIUM IS ACHIEVED WHEN DRIVING FORCES ARE EQUAL EVERYWHERE:

THERMAL: $\quad T^\alpha = T^\beta$

MECHANICAL: $\quad P^\alpha = P^\beta$

More on the relationship between chemical potential and Gibbs free energy

- Last time, we introduced partial molar quantities: the analog of molar quantities for multicomponent systems. Remember that partial molar quantities are directly related to the total thermodynamic function for the system. Thus we have two ways to write out the 'integrated' form of the Gibbs free energy, for example:

'INTEGRATED' GIBBS FREE ENERGY:

$$G \equiv U - (-PV) - TS = H - TS$$

OR, USING DEF'N OF PARTIAL MOLAR QUANTITIES:

$$\boxed{I} \quad G = \sum_{i=1}^{C} n_i \bar{G}_i = \sum_{i=1}^{C} n_i \mu_i$$

IF I HAVE A PURE COMPONENT (C=1):

$$G = n\mu$$

$$\mu = \frac{G}{n} = \bar{G} = \bar{H} - T\bar{S}$$

CHEMICAL POTENTIAL **IS** THE MOLAR FREE ENERGY IN A PURE SYSTEM

Chemical potentials in multicomponent systems are linked: the Gibbs-Duhem equation

'DIFFERENTIAL' FORM OF G: $dG = -SdT + VdP + \sum_{i=1}^{C} \mu_i dn_i$

AT CONST. T, P: $dG = \sum_{i=1}^{C} \mu_i dn_i$

LET C=2: $dG = \mu_A dn_A + \mu_B dn_B \quad \boxed{II}$

FROM $\boxed{I}$: $dG = n_A d\mu_A + \mu_A dn_A + n_B d\mu_B + \mu_B dn_B \quad \boxed{III}$

EQUATE $\boxed{II}$ AND $\boxed{III}$: $\mu_A dn_A + \mu_B dn_B = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$

$$n_A d\nu_A + n_B dN_B = 0$$

GIBBS - DUHEM
EQUATION

$$d\nu_A = -\frac{n_B dN_B}{n_A}$$

The chemical potential of the ideal gas

Models of the chemical potential in materials

- So far we've derived rules that the chemical potential must obey in the approach toward equilibrium, but we haven't provided any equations that tell us what goes into the chemical potential. Because the chemical potential embodies chemical forces within materials, it is different for every material. However, several models for the chemical potential have been developed, which are the basis of many first-order calculations in materials science & engineering. **Note that in some cases, we can calculate chemical potentials from first-principles quantum mechanics calculations (for example, this can even be done by hand for simple gases).** These models will allow us to make predictions for the behavior of multi-component materials.

The ideal gas model

- A starting point for models of the chemical potential is to consider perhaps the theoretically simplest form of matter- the ideal gas. We stated that the ideal gas is modeled by two fundamental relationships:

$$PV = nRT \qquad\qquad U = U(T) = \frac{3}{2}nRT$$

- Using only the ideal gas equation of state, we can derive the chemical potential of the ideal gas. Consider that we have a quantity of a pure ideal gas in a closed system. As we showed above, the chemical potential is the molar free energy of the gas:

$$\mu = \overline{G} \qquad\qquad dG = VdP - SdT + \sum_{i=1}^{c} \mu_i dn_i$$

$$d\mu = d\overline{G} = \overline{V}dP - \overline{S}dT \qquad\qquad 0 \quad \text{CLOSED} \\ C=1 \\ P=1$$

- Now, for any state function, we can integrate a differential:

$$dX \rightarrow \int_{initial}^{final} dX = \Delta X = X_{final} - X_{initial}$$

- If we integrate our differential for the chemical potential, we can calculate the chemical potential in some arbitrary state relative to that in some other defined reference state. We will proceed in the following way: We want to know the chemical potential at a temperature T and pressure P, relative to a reference state of the gas at the same temperature (T) and a reference pressure, P_o. Integrating the expression above:

$$\text{FIXED } T: \qquad d\mu = \overline{V}dP$$

$$d\mu = \boxed{\overline{V}\,dP} = \frac{RT}{P}\,dP$$

IDEAL GAS:

$$\overline{V} = \frac{V}{n} = \frac{RT}{P}$$

INTEGRATE BOTH SIDES:

CURRENT STATE: T, P

$$\int d\mu = \Delta\mu = \mu(T,P) - \mu^{o}(T) = \int \frac{RT}{P'}\,dP'$$

REF. STATE:

$$T, P_o = 1\,atm$$

$$\boxed{\mu(T,P) = \mu^{o}(T) + RT \ln \frac{P}{P_o}} \quad \begin{array}{l} \text{CHEMICAL} \\ \text{POTENTIAL OF} \\ \text{IDEAL GAS} \\ \text{(PURE)} \end{array}$$

$$P_o = 1\,atm$$

- Very commonly, the reference state pressure is taken as P_o = 1 atm.

ACCESS TO OTHER QUANTITIES:

$$d\overline{G} = \boxed{-\overline{S}\,dT} + \overline{V}\,dP$$

$$= \left(\frac{\partial\overline{G}}{\partial T}\right)_{P,n} dT + \left(\frac{\partial\overline{G}}{\partial P}\right)_{T,n} dP$$

$$\overline{S}(T,P) = ? = -\left(\frac{\partial\overline{G}}{\partial T}\right)_{P,n}$$

$$\overline{S} = -\left(\frac{\partial\mu}{\partial T}\right)_{P,n} = -\left(\frac{\partial\mu^{o}(T)}{\partial T}\right)_{P,n} - R\ln\frac{P}{P_o}$$

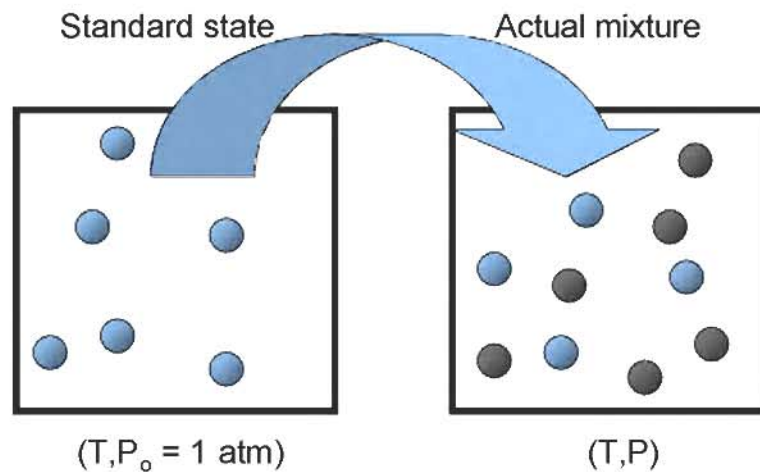IDEAL GAS $\qquad \overline{S}^{o}(T)$

$$\boxed{\overline{S}(T,P) = \overline{S}^{o}(T) - R\ln\frac{P}{P_o}}$$

Chemical potential of ideal gas mixtures

- A straightforward extension of the calculation we have just performed is to determine the chemical potential in an ideal gas mixture. The situation is illustrated by the cartoon below:

Standard state   Actual mixture

$(T, P_o = 1 \text{ atm})$ (T, P)

- Pressure is proportional to concentration for gases ($P/RT = n/V$ for ideal gases). To describe ideal gas mixtures, we introduce the concept of **partial pressure**:

$$\text{PARTIAL PRESSURE} = P_i = X_i P$$

TOTAL PRESSURE

MOLE FRACTION i

$$P = \sum_{i=1}^{c} P_i = \sum_{i=1}^{c} X_i P$$

IDEAL GASES ARE UNAFFECTED BY THE PRESENCE OF ONE ANOTHER

WHAT IS μ IN GAS MIXTURE?

$$\int_{T, P_o \text{ PURE GAS}}^{T, P_i \text{ IN GAS MIXTURE}} d\mu = \Delta\mu = \mu_i(T, P) - \mu_i^0(T) = \int_{P_o = 1 \text{ atm}}^{P_i} \frac{RT}{P} dP$$

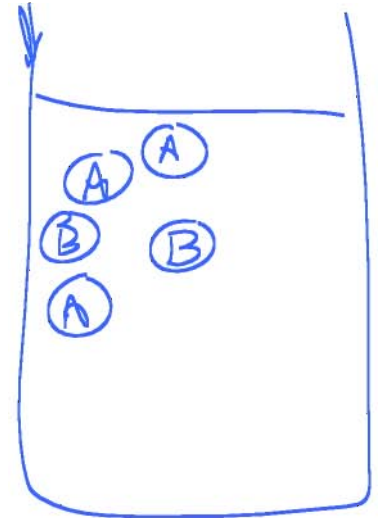$$\therefore \boxed{\mu_i(T, P) = \mu_i^0(T) + RT \ln \frac{P_i}{P_o}}$$

The general solution model

- The simple ideal gas model of the chemical potential above can be extended for use in describing general solid, liquid, or gaseous solutions.

- In the general solution model, the chemical potential is given by:

$$\mu_i(T, P, X_i) = \mu_i^o(T) + RT \ln a_i$$

↑ MOLE FRACTION i

↑ ACTIVITY OF i

- ○ The chemical potential of component i is a function of its mole fraction, the pressure, and the temperature.

- ○ To calibrate the value of the chemical potential in a given state, it is standard practice to refer to the chemical potential of that state relative to the pure component i in some reference state (typically atmospheric pressure). The first term is the chemical potential of the component in its reference state:

$$\mu_i^o(T) = \text{CHEMICAL POTENTIAL OF PURE } i \text{ AT TEMP. } T \text{ AND } P = 1 \text{ atm (CONVENTIONAL STANDARD STATE)}$$

  - ▪ …which emphasizes that the term *RT log a_i* quantifies the difference between the chemical potential of i in its current state from that of pure i in its reference state.

- ○ In addition to the reference state, we've also introduced a new quantity a_i- the activity of component i. The activity is further defined by introducing a second new quantity γ_i, the activity coefficient:

$$a_i \equiv \gamma_i X_i$$
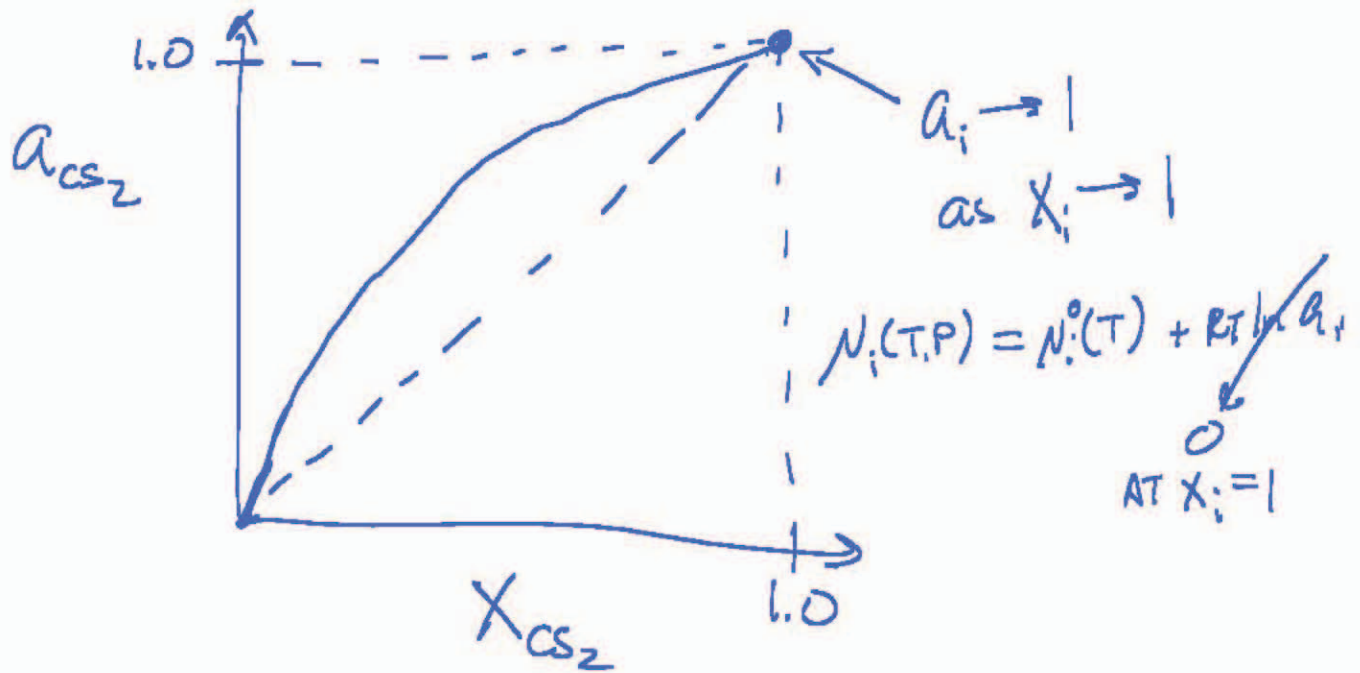
← MOLE FRACTION i

↳ ACTIVITY COEFFICIENT → VARIES W/CHEMISTRY/ BONDING

- When we introduce statistical mechanics in the second half of the course, we will see how simple microscopic models of how the atoms and molecules in a material interact can give rise to the general solution model form of the chemical potential.

$$\mu_i(T, P, X_i) = \mu_i^o(T) + RT \ln \gamma_i X_i$$

- Both activity and activity coefficient may vary as a function of the mole fraction of each species in the solution. Shown below are experimental data for a solution of CS_2 in acetone from the text:

$$a_i \rightarrow 1$$
$$\text{as } X_i \rightarrow 1$$

$$\mu_i(T,P) = \mu_i^o(T) + RT \ln a_i$$

$$\text{AT } X_i = 1$$

Ideal solutions

- When the activity coefficient $\gamma_i = 1$, the activity is equal to the mole fraction and the chemical potential reduces to:

$$\mu_i = \mu_i^0 + RT \ln \gamma_i X_i$$

$$\text{IDEAL SOLUTION:} \quad \boxed{\mu_i(T,P) = \mu_i^0(T) + RT \ln X_i}$$

- Systems where this approximation holds are known as *ideal solutions*. The ideal solution model describes the chemical potential of any real very dilute solution.

References

1.   Carter, W. C. *3.00 Thermodynamics of Materials Lecture Notes*   (2002).