University of Washington
Department of Chemistry
Chemistry 452/456
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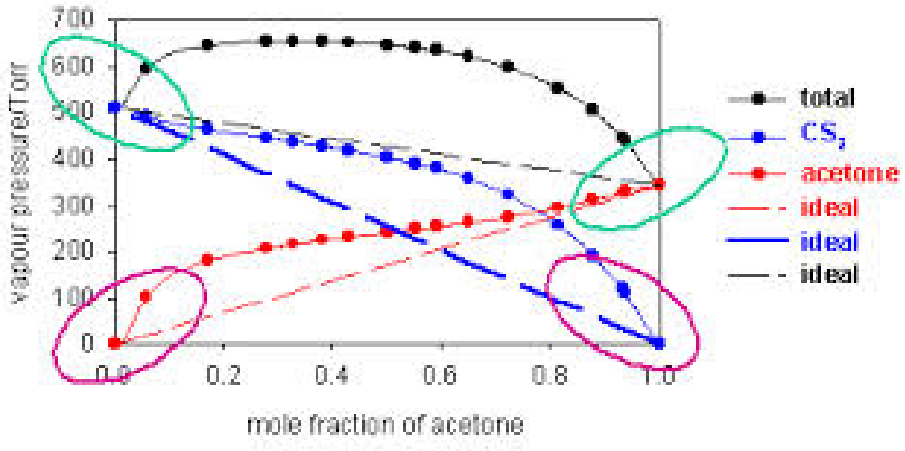
Lecture 16 8/04/14

A. Real Vapors and Fugacity

- Henry's Law accounts for the properties of extremely dilute solution. As shown in Figure 1 Henry's Law only accounts for the properties of solutions in the encircled areas.

- For solutions that are not dilute, the physical properties of these solutions starting with their chemical potentials, is not accurately described by either Raoult's Law or Henry's Law. To accurately describe the free energy of a concentrated solution of a non-ideal vapor in contact with a non-deal, concentrated solution of a non-electrolyte, the concept of activity is introduced.

Figure 1: The vapor pressure above mixtures of of CS2 and acetone deviate strongly from both Raoult's Law (dashed lines) and Henry's Law (encircled areas) for mole fractions between 0.2 and 0.8.



- In the two simple solution models we have convered we assumed the vapor behaves ideally so that the chemical potential of each component in the vapor phase is obtained by a simple integration...

$$d\mu_i(v) = \bar{V}_i dP_i = \frac{RT}{P_i} dP_i$$
$$\therefore \mu_i(v) - \mu_i^0 = RT \ln\left(\frac{P_i}{P_i^0}\right) \qquad (16.1)$$

- If

- $$\frac{V}{n} \neq \frac{RT}{P} \; or \; \bar{V} = \frac{V}{n} = \frac{RT}{P} + \alpha \qquad (16.2)$$

where α is an empirical correction term intended to account for all effects (i.e. intermolecular interactions, finite molecular size etc.) that cause deviations from ideal gas behavior. .

- The expression for the chemical potential of the vapor is now

$$d\mu_i(v) = \bar{V}dP = \frac{RT}{P}dP + \alpha dP \Rightarrow \mu_i(v) - \mu_i^0 = RT\int_{P_i^0}^{P_i}\frac{dP}{P} + \int_{P_i^0}^{P_i}\alpha dP$$

- $$\therefore \mu_i(v) - \mu_i^0 = RT\ln\left(\frac{P_i}{P_i^0}\right) + \int_{P_i^0}^{P_i}\alpha dP \qquad (16.3)$$

- If we know the equation of state a can be determined explicitly. Otherwise a can be measured directl as a function of P and the integral can be evaluated numerically. See examples below.

- In analog with the ideal vapor expression $\mu_i^{vap} - \mu_i^{vap,0} = RT\ln\left(\frac{P_i}{P_i^0}\right)$, for a real vapor we define the fugacity f. The fugacity is the vapor pressure...or escape tendency... corrected for the fact that the gas is not ideal.

$$d\mu = RTd\ln f = \frac{RT}{P}dP + \alpha dP = RTd\ln P + \alpha dP$$
$$\therefore RTd\ln f = RTd\ln P + \alpha dP \Rightarrow d\ln f = d\ln P + \frac{\alpha}{RT}dP \qquad (16.4)$$

- The reference state can be defined as the limit of very low pressure where the vapor behaves ideally and so f_0=P_0. We obtain…

$$\int_{f_i^0}^{f_i} d\ln f_i \approx \int_{P_i^0}^{f_i} d\ln f_i = \int_{P_i^0}^{P_i} d\ln P + \frac{1}{RT}\int_{P_i^0}^{P_i}\alpha dP$$
$$\therefore \ln\left(\frac{f}{P_i^0}\right) = \ln\left(\frac{P_i}{P_i^0}\right) + \frac{1}{RT}\int_{P_i^0}^{P_i}\alpha dP \qquad (16.5)$$

- We can rearrange equation 16.5 and after a little algebra we get

$$f_i \approx P_i \exp\left\{\frac{1}{RT}\int_{P_i^0}^{P}\alpha dP\right\} = \gamma_i^f P_i \qquad (16.6)$$

where γ_f is the fugacity coefficient. The lower limit of the integration approaches zero in many practical applications.

- The fugacity coefficient can be determined by measuring the quantity $\bar{V} - \frac{RT}{P} = \alpha$ over a range of pressures and determining the integral $\int_{P^0}^{P}\alpha dP$ numerically.

- Note that γ_f measures the degree to which the component of the vapor deviates from the ideal gas law at P_i and P_i^0. Therefore

$$\lim_{P_i \to 0}\left(\frac{f_i}{P_i}\right) = 1 \; or \; \lim_{P_i \to 0}\left(\gamma_i^f\right) = 1 \tag{16.7}$$

B. Examples of Fugacity Calculations

- Example 1: If the equation of state is known the fugacity can be determined by deriving the quantity α from the equation of state. Suppose the equation of state is

$$P\left(V - nb\right) = nRT \tag{16.8}$$

where b is a constant that reflects the volume excluded by finite molecules in the gas phase. Solve for V/n: $\frac{V}{n} = \bar{V} = \frac{RT}{P} + b$. Then α=b and the fugacity coefficient is easy to calculate. Assuming for convenience that $P_i^0 << P_i$

$$\gamma_f = \exp\left\{\frac{1}{RT}\int_{P_i^0}^{P_i} \alpha dP_i\right\} = \exp\left\{\frac{b}{RT}\int_{P_i^0}^{P} dP_i\right\} = e^{b\left(P_i - P_i^0\right)/RT} \approx e^{bP_i/RT} \tag{16.9}$$

All you need to calculate the fugacity is the pressure P and the value for b.

- Note in some texts the fugacity is defined a little differently. Suppose we define the fugacity as

$$\begin{aligned} P\bar{V} &= RT + \alpha \; or \; \bar{V} = \frac{RT}{P} + \frac{\alpha}{P} \\ \therefore d\mu_i &= RT \ln f_i = RTd \ln P_i + \frac{\alpha}{P} dP_i \\ \therefore d \ln f_i &= d \ln P_i + \frac{1}{RT}\frac{\alpha}{P_i} dP_i \\ \therefore f_i &= P_i \exp\left[\frac{1}{RT}\int_{P_i^0}^{P_i} \frac{\alpha}{P_i} dP \right]_i \end{aligned} \tag{16.10}$$

- This alternative definition makes no difference to the result. Again for $P\left(V - nb\right) = nRT$ we now get with the alternative definition $\alpha = bP_i$. But we get the same final result as we did using the other definition:

$$\begin{aligned} f_i &= P_i \exp\left[\frac{1}{RT}\int_{P_i^0}^{P_i} \frac{\alpha}{P_i} dP_i \right]_i = P_i \exp\left[\frac{1}{RT}\int_{P_i^0}^{P_i} \frac{bP_i}{P_i} dP_i \right]_i \\ &= P_i \exp\left[\frac{b\left(P_i - P_i^0\right)}{RT}\right] \approx P_i e^{bP_i/RT} \end{aligned} \tag{16.11}$$

- Example 2: The fugacity can also be calculated from experimental data using the equation $\alpha = \bar{V}_i - \frac{RT}{P_i}$ o r $\alpha = P_i\bar{V}_i - RT$. Below is a study of the fugacity of nitrogen gas as a function of pressure. Noteworthy features:
- The quantity $\frac{\bar{V}_i}{RT} - \frac{1}{P_i} = \frac{1}{RT}\frac{\alpha}{P_i}$ is tabulated in the second column and plotted as a function of pressure.
- Note the area under the curve is

$$\ln \gamma_i^f = \frac{1}{RT}\int_{P_i\sim 0}^{P_i=800\,atm} \frac{\alpha}{P_i}\,dP_i$$

- The third column is the fugacity coefficient explicitly and the degree to which F/P deviates from 1 measures the deviation from ideal gas behavior.
- The fourth column tests the degree to which the data fits a model $P(V-nb) = nRT$ where bP<<RT . The closer the value in column 4 is to 1 the closer is the agreement to the model.

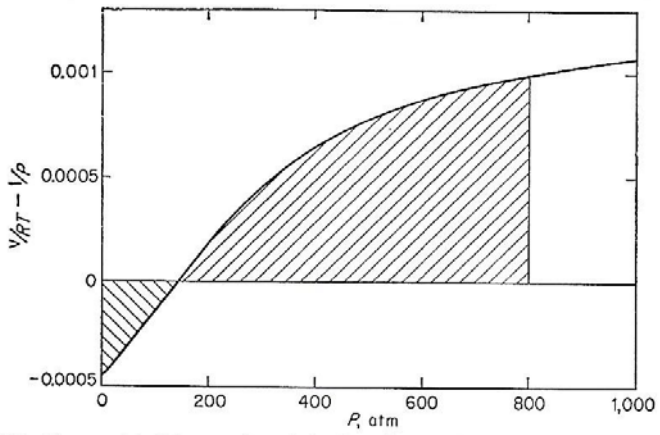


FIG. 16-2. The graphical integration of the fugacity of N_2 at 800 atm. The data are for 0°C.

TABLE 16-1. THE FUGACITY OF NITROGEN AT 0°C†

P, atm	$\frac{v}{RT} - \frac{1}{P}$	$\frac{f}{P}$	$\frac{Pv}{RT} = \frac{P}{P_i}$
1	−0.00045	0.99955	0.99955
10	−0.00043	0.9956	0.9957
50	−0.00030	0.9812	0.9850
100	−0.000146	0.9703	0.9854
150	+0.000020	0.9672	1.0030
200	0.000181	0.9721	1.0363
300	0.000451	1.0055	1.1353
400	0.000641	1.062	1.2566
600	0.000874	1.239	1.5242
800	0.000995	1.495	1.7964
1000	0.001070	1.839	2.070

C. Real Solution Equation of State

- To account for non-ideality of the vapor above a real solution, we substitute the fugacity for the pressure. We also introduce the term activity, assumed to be the ratio of the fugacity at a given pressure to the fugacity at a reference pressure;

$$\frac{f_i}{f_i^0} = a_i \qquad (16.12)$$

- If the solution were ideal the activity would just be the mole fraction of component I in the solution. But in analogy to the fugacity coefficient, deviations from ideality are reflected in a activity coefficient:

$$\frac{f_i}{f_i^0} = a_i = \gamma_i x_i \qquad (16.13)$$

- Equation 16.13 is the equation of state for real solutions. Like the fugacity coefficient, the activity coefficient can be measured directly or calculated if a model for the real solution is available. We will consider a real solution model in the next lecture, called the regular solution model. In the next section we show how activity and fugacity are introduced into equilibrium constant expressions.

D. Summary of Equilibrium Relationships for Chemical Reactions with Real Vapors and Real Solutions (non-Electrolyte)

- Consider a reaction $\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$ where a, b, c, and d are stoichiometric coefficients. The condition for equilibrium is:

$$\nu_A \mu_A + \nu_B \mu_B = \nu_C \mu_C + \nu_D \mu_D$$

$$\therefore \nu_A \left(\mu_A^{\bullet} + RT \ln a_A \right) + \nu_B \left(\mu_B^{\bullet} + RT \ln a_B \right) = \nu_C \left(\mu_C^{\bullet} + RT \ln a_C \right) + \nu_D \left(\mu_D^{\bullet} + RT \ln a_D \right)$$

- We now rearrange the equation:

$$-\Delta G^0 = \nu_A \left(\mu_A^{\bullet} \right) + \nu_B \left(\mu_B^{\bullet} \right) - \nu_C \left(\mu_C^{\bullet} \right) - \nu_D \left(\mu_D^{\bullet} \right) = -\nu_A \left(RT \ln a_A \right) - \nu_B \left(RT \ln a_B \right) + \nu_C \left(RT \ln a_C \right) + \nu_D \left(RT \ln a_D \right)$$

$$\therefore \Delta G^0 = -RT \left[\ln a_A^{-\nu_A} + \ln a_B^{-\nu_B} \ln a_C^{\nu_C} \ln a_D^{\nu_D} \right] = -RT \ln \left[\frac{a_C^{\nu_C} a_D^{\nu_D}}{a_A^{\nu_A} a_B^{\nu_B}} \right]$$

- In general $K = \dfrac{a_C^{\nu_C} a_D^{\nu_D}}{a_A^{\nu_A} a_B^{\nu_B}}$ where a_i is the activity of species i.
- Ideal Gases: $a_i = \dfrac{P_i}{P_i^0} \Rightarrow K_P = \left(\dfrac{P_C}{P_C^0} \right)^{\nu_C} \left(\dfrac{P_D}{P_D^0} \right)^{\nu_D} \left(\dfrac{P_A^0}{P_A} \right)^{\nu_A} \left(\dfrac{P_B^0}{P_B} \right)^{\nu_B}$
- Real Gases: $a_i = \dfrac{f_i}{f_i^0} \Rightarrow K_f = \left(\dfrac{f_C}{f_C^0} \right)^{\nu_C} \left(\dfrac{f_D}{f_D^0} \right)^{\nu_D} \left(\dfrac{f_A^0}{f_A} \right)^{\nu_A} \left(\dfrac{f_B^0}{f_B} \right)^{\nu_B}$
- Non-electrolyte Solutions, Ideal, units of concentration:

$$a_i = \frac{C_i}{C_i^0} \Rightarrow K_C = \left(\frac{C_C}{C_C^0} \right)^{\nu_D} \left(\frac{C_D}{C_D^0} \right)^{\nu_D} \left(\frac{C_A^0}{C_A} \right)^{\nu_A} \left(\frac{C_B^0}{C_B} \right)^{\nu_B}$$

- Non-electrolyte Solutions, Ideal, units of molality:

$$a_i = \frac{m_i}{m_i^0} \Rightarrow K_m = \left(\frac{m_C}{m_C^0}\right)^{\nu_C} \left(\frac{m_D}{m_D^0}\right)^{\nu_D} \left(\frac{m_A^0}{m_A}\right)^{\nu_A} \left(\frac{m_B^0}{m_B}\right)^{\nu_B}$$

- Non-electrolyte Solutions, Real, units of molality:

$$a_i = \frac{\gamma_i m_i}{m_i^0} \Rightarrow K_m = \left(\frac{\gamma_C m_C}{m_C^0}\right)^{\nu_C} \left(\frac{\gamma_D m_D}{m_D^0}\right)^{\nu_D} \left(\frac{m_A^0}{\gamma_A m_A}\right)^{\nu_A} \left(\frac{m_B^0}{\gamma_B m_B}\right)^{\nu_B}$$

where all activities correspond to equilibrium conditions.