Chemistry 163B

μ_i and $\Delta\mu_{reaction}$

Activity

Equilibrium

goals

- Derive equilibrium and spontaneity criteria applying multicomponent thermodynamic relationships; i.e chemical potential ($\Delta\mu_{reaction}$)
- Define concentration dependence of μ in terms of **activity** (fugacity) of 'real' gases, actual solutes
- Apply **activity** to equilibrium K_{eq}
- Derive how to obtain fugacity if **REAL** gas

equilibrium in terms of $\Delta\mu$

$$n_A\, A + n_B\, B \longrightarrow n_C\, C + n_D\, D$$

$$\nu_A = -n_A \quad \nu_B = -n_B \quad \nu_C = +n_C \quad \nu_D = +n_D$$

$d\xi$ is extent of reaction
$d\xi > 0$ forward reaction
$d\xi < 0$ reverse reaction

$$dn_i = \nu_i\, d\xi$$

$dn_i > 0$ substance *i* increases
$dn_i < 0$ substance *i* decreases

equilibrium in terms of $\Delta\mu$

$$dG_{T,P} < 0 \text{ spontaneous}$$

$$dG_{T,P} = 0 \text{ equilibium}$$

whole pot of mixed reactants and products

$$dG = -SdT + VdP + \sum_{i=1}^{N} \mu_i dn_i$$

$$dn_i = \nu_i d\xi$$

$$dG = -SdT + VdP + \sum_{i=1}^{N} \mu_i \nu_i \, d\xi$$

$$dG_{T,P} = \left(\sum_{i=1}^{N} \mu_i \nu_i \right) d\xi \leq 0$$

equilibrium in terms of Δμ

$$dG_{T,P} = \underbrace{\left(\sum_{i=1}^{N} \mu_i \nu_i \right)}_{?} d\xi \le 0$$

$$dG_{T,P} = \underbrace{\left(\sum_{i=1}^{N} \mu_i \nu_i \right)}_{\Delta\mu_{reaction}} d\xi \le 0$$

$$dG_{T,P} = \Delta\mu_{reaction} d\xi \le 0$$

$\Delta\mu_{reaction} < 0$ forward reaction spontaneous ($d\xi > 0$)

$\Delta\mu_{reaction} > 0$ reverse reaction spontaneous ($d\xi < 0$)

$\Delta\mu_{reaction} = 0$ equilibrium

just like ΔG !!!

concentration dependence of μ_i

ideal gas, one component (pure substance)

$$\bar{G} = \bar{G}^\circ + RT\, ln\left(\frac{P}{1\, bar}\right)$$

led to

$$\Delta G_{reaction} = \Delta G^\circ_{reaction} + \underline{R}T\, ln(Q_P)$$

what about if other species present?

$$\mu_i = \mu_i^\circ + RT\, ln\left(\frac{P_i}{1\, bar}\right)$$

$$\Delta\mu_{reaction} = \Delta\mu^\circ_{reaction} + \underline{R}T\, ln Q_P$$

$$\Delta\mu^\circ_{reaction} = \sum_i \nu_i \mu_i^\circ \quad Q_P = \prod_i \left(\frac{P_i}{1\, bar}\right)^{\nu_i}$$

HANDOUT #45

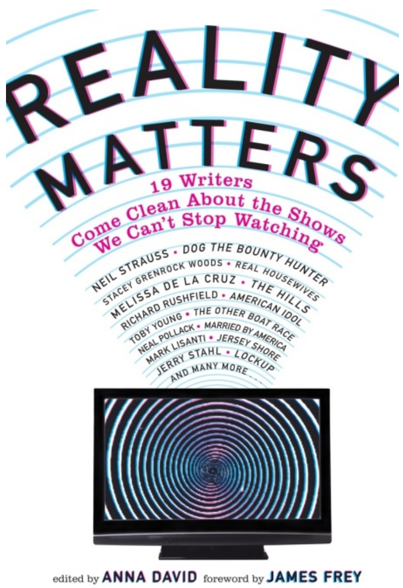
yada -yada- yada: and so forth for $\Delta\mu_{reaction}$

$$\Delta\mu^{\circ}_{reaction} = -\underline{R}T \ln K_P$$

$$\left(\frac{\partial \frac{\Delta\mu}{T}}{\partial T}\right)_P = -\frac{\Delta H}{T^2} \quad \textit{where} \quad \Delta H = \sum_i \nu_i \bar{H}_i = \sum_i \nu_i \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_j \neq n_i}$$

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H^{\circ}}{\underline{R}T^2} \quad \textit{where} \quad \Delta H^{\circ} = \sum_i \nu_i \bar{H}^{\circ}_i$$

correcting for REALITY (activity and fugacity)



correcting for REALITY (activity and fugacity)

- will define activity and fugacity coefficients γ_i's that provides corrections for the deviation of chemical potential from the ideal gas and solute concentration dependence

- activity and fugacity coefficients are obtained from experimental measurements on REAL systems
or by theory (Debye-Huckel)

more general μ_i and corrections for non-ideality (~E&R eqn 9.50, p227)$_{3rd}$

$$\mu_i(T) = \mu_i^\circ(T) + RT\,ln\left(a_i / a_i^0 \right)$$

standard conditions

how μ_i 'really' changes in going from standard conditions to actual conditions

$$a_i = activity\ of\ component\ i$$

$$a_i = \gamma_i \times \left[ideal\ measure\ of\ pressure, concentration, etc \right]$$

γ_i is activity coefficient, a correction for non-ideality

$$a_i^o = 1 \quad unit \quad (bar, molar, etc)$$

more general μ_I and corrections for non-ideality

$$\Delta\mu_{reaction} = \Delta\mu^{o} + \underline{R}T\ \ln Q$$

where now Q is written in terms of activities

$$Q = \prod_i \underbrace{\left(\frac{a_i}{a_i^{\circ}}\right)}_{unitless}^{\bar{\nu}_i} \qquad Q = \underbrace{\frac{(a_C)^{\bar{n}_C}(a_D)^{\bar{n}_D}}{(a_A)^{\bar{n}_A}(a_B)^{\bar{n}_B}}}$$

dropped the $a_i^{\circ} = 1$ 'unit'
but Q is 'unitless'

fugacity of gases

1. GASES:

$$a_i = f_i = \gamma_i \, P_i$$

- f_i: fugacity of gas
- γ_i: fugacity coefficient
- P_i: partial pressure

$$Q = \frac{(a_C)^{\bar{n}_C}(a_D)^{\bar{n}_D}}{(a_A)^{\bar{n}_A}(a_B)^{\bar{n}_B}}$$

$$Q = \frac{\left(\gamma_C \dfrac{P_c}{1bar}\right)^{\bar{n}_C}\left(\gamma_D \dfrac{P_D}{1bar}\right)^{\bar{n}_D}}{\left(\gamma_A \dfrac{P_A}{1bar}\right)^{\bar{n}_A}\left(\gamma_B \dfrac{P_B}{1bar}\right)^{\bar{n}_B}}$$

$$Q = \left(\frac{\gamma_C^{\bar{n}_C}\gamma_D^{\bar{n}_D}}{\gamma_A^{\bar{n}_A}\gamma_B^{\bar{n}_B}}\right)\frac{\left(\dfrac{P_C}{1bar}\right)^{\bar{n}_C}\left(\dfrac{P_D}{1bar}\right)^{\bar{n}_D}}{\left(\dfrac{P_A}{1bar}\right)^{\bar{n}_A}\left(\dfrac{P_B}{1bar}\right)^{\bar{n}_B}} = \underline{\underline{\gamma}}\, Q_P$$

- $\underline{\underline{\gamma}}$: correction for non-ideality
- Q_P: ideal gas Q_P

other conventions for activities

2. pure solids and liquids

$$\mu_i(T,P) \approx \mu_i^{\circ}(T,P=1bar)$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = \bar{V}_i \quad \text{(small for liquid or solid)}$$

so $a_i \approx 1$ *for pure solid or liquid*

[unless extreme pressure]

other conventions for activities

3. solutes in solutions

$$a_i = \gamma_i \left[I \right]$$

concentration of I, usually molar but may be X_i

activity coefficient γ_i corrects 'ideal' measure of 'concentration

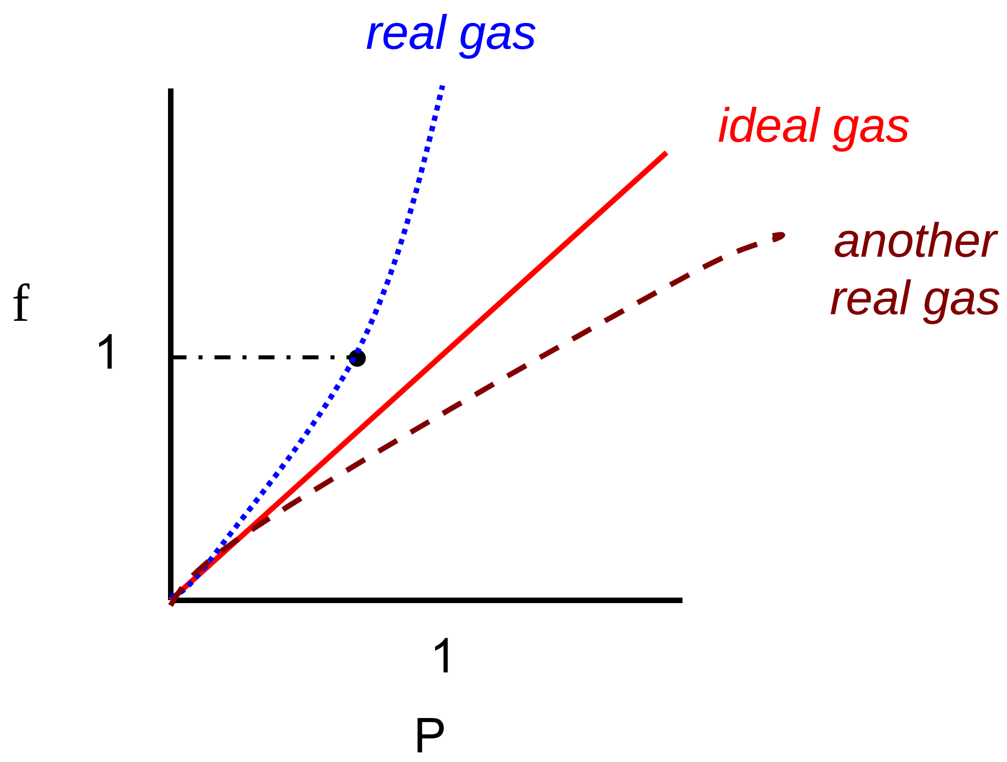
if "activity coefficients unity"

$$a_i = \left[I \right] \qquad a_i \equiv f_i = P_i \qquad a_i = 1$$

solute *gas* *pure liquid or solid*

HW#7 γ=1 except prob. 41* and 43.

*how to evaluate activity (fugacity) coefficients for real gases (HW7 #*41)*



how to evaluate activity (fugacity) coefficients for real gases

$$\left(\frac{\partial \mu}{\partial P}\right)_{T,n} = \bar{V} \quad \textit{and}$$

$$\mu = \mu^{\circ} + RT \ln f$$

need in a moment

$$\left(\frac{\partial \mu}{\partial P}\right)_{T,n} = RT\left(\frac{\partial \ln f}{\partial P}\right)_{T,n}$$

$$\textit{so} \quad RT\left(\frac{\partial \ln f}{\partial P}\right)_{T,n} = \bar{V}$$

expression for $d\ln\left(\frac{f}{P}\right)$ will prove useful

$$\left(\frac{\partial \ln\left(\frac{f}{P}\right)}{\partial P}\right)_{T,n} = \left(\frac{\partial\left(\ln f - \ln P\right)}{\partial P}\right)_{T,n} = \left(\frac{\partial \ln f}{\partial P}\right)_{T,n} - \left(\frac{\partial \ln P}{\partial P}\right)_{T,n}$$

$$= \frac{1}{RT}\bar{V} - \frac{1}{P} = \frac{1}{RT}\left(\bar{V} - \frac{RT}{P}\right)$$

how to evaluate activity (fugacity) coefficients for real gases

$$\int_{P_1}^{P} d\left(ln\frac{f}{P'}\right) = \int_{P_1}^{P}\frac{1}{RT}\left(\bar{V} - \frac{RT}{P'}\right)dP'$$

$$ln\left(\frac{f(P)}{P}\right) - ln\left(\frac{f(P_1)}{P_1}\right) = \frac{1}{RT}\int_{P_1}^{P}\left(\bar{V} - \frac{RT}{P'}\right)dP'$$

$$ln\left(\frac{f(P)}{P}\right) = ln\left(\frac{f(P_1)}{P_1}\right) + \frac{1}{RT}\int_{P_1}^{P}\left(\bar{V} - \frac{RT}{P'}\right)dP'$$

$P_1 \longrightarrow 0$

$$\frac{f(P_1)}{P_1} \rightarrow 1$$

$$ln\left(\frac{f(P_1)}{P_1}\right) \rightarrow 0$$

$$\left(\bar{V}_{ACTUAL} - \bar{V}_{IDEAL\ GAS}\right)$$

*how to evaluate activity (fugacity) coefficients for real gases (eqn 7.20 E&R and HW7 #*41)*

$$\ln f(P) = \ln P + \frac{1}{RT}\int_{P_1\to 0}^{P}\left(\bar{V} - \frac{RT}{P'}\right)dP' = \ln P + \frac{1}{RT}\int_{P_1\to 0}^{P}\left(\bar{V}_{ACTUAL} - \bar{V}_{IDEAL\,GAS}\right)dP'$$

$$\ln\left(\frac{f(P)}{P}\right) = \ln(\gamma) = \frac{1}{RT}\int_{P_1\to 0}^{P}\left(\bar{V} - \frac{RT}{P'}\right)dP' = \frac{1}{RT}\int_{P_1\to 0}^{P}\left(\bar{V}_{ACTUAL} - \bar{V}_{IDEAL}\right)dP'$$

$$z = \frac{\bar{V}_{actual}}{\bar{V}_{ideal}} = \frac{P\bar{V}_{actual}}{RT} \quad \textit{(compression factor E\&R eqn. 7.6)}$$

$$\ln\gamma = \frac{1}{RT}\int_{P_1\to 0}^{P}\bar{V}_{ideal}(z-1)dP' = \int_{P_1\to 0}^{P}\frac{(z-1)}{P'}dP'$$

HW7 41*

$$\gamma(P,T) = \exp\left[\int_{P_1\to 0}^{P}\frac{z-1}{P'}dP'\right] \quad (E\ \&\ R\ eqn\ 7.21)$$

End of Lecture