Chemistry 163B
μ_i and $\Delta\mu_{reaction}$
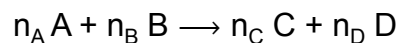
Activity

Equilibrium

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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

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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

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equilibrium in terms of $\Delta\mu$

$dG_{T,P} < 0$ spontaneous

$dG_{T,P} = 0$ equilibium

whole pot of mixed reactants and products

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

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

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

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equilibrium in terms of $\Delta\mu$

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

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

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

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

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

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

just like ΔG !!!

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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

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

what about if other species present?

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

HANDOUT #45

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

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

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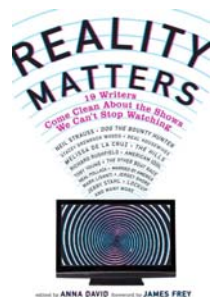*yada -yada- yada: and so forth for $\Delta\mu_{reaction}$*

$$\Delta\mu_{reaction}^{\circ} = -\underline{R}T\,ln\,K_P$$

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

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

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correcting for REALITY (activity and fugacity)

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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)

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

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

*standard
conditions*

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

$a_i = $ *activity of component i*

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

γ_i is activity coefficient, a correction for non-ideality

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

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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*

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

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

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fugacity of gases

1. GASES:

$$a_i = f_i = \gamma_i\,P_i \quad \leftarrow \text{partial pressure}$$

fugacity of gas   *fugacity coefficient*

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

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

correction for non-ideality

ideal gas Q_P

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

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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]

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other conventions for activities

3. solutes in solutions

$$a_i = \gamma_i [I]$$

concentration of I, usually molar but may be X_i

activity coefficient γ_i corrects 'ideal' measure of 'concentration

if "activity coefficients unity"

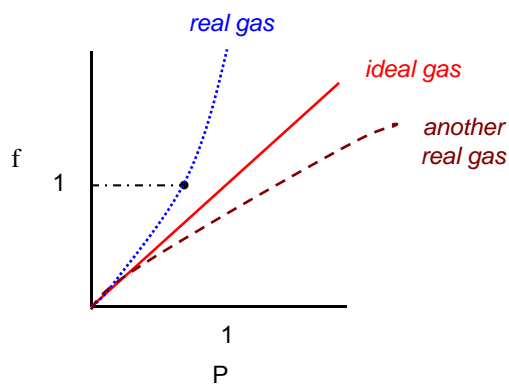$$a_i = [I] \qquad a_i \equiv f_i = P_i \qquad a_i = 1$$

solute   gas   pure liquid or solid

HW#7 $\gamma=1$ except prob. 41* and 43.

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

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how to evaluate activity (fugacity) coefficients for real gases

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

$$\mu = \mu^\circ + RT \ln f \qquad \boxed{\textit{need in a moment}}$$

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

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

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

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

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

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how to evaluate activity (fugacity) coefficients for real gases

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

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

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

$$P_1 \longrightarrow 0$$
$$\frac{f(P_1)}{P_1} \to 1$$
$$ln\left(\frac{f(P_1)}{P_1} \right) \to 0$$

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

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

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

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

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

$$\ln\gamma = \frac{1}{RT}\int_{P_1\to 0}^{P} \bar{V}_{ideal}(z-1)dP' = \int_{P_1\to 0}^{P}\frac{(z-1)}{P'}dP' \qquad \boxed{\text{HW7 41*}}$$

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

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End of Lecture

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