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Lecture 17
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 (effective pressure) of **REAL** gas

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spontaneity and equilibrium in terms of $\Delta\mu$

$$n_A A + n_B B \rightleftharpoons n_C C + n_D D$$

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

$d\xi$ 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

e.g. i ="products" $\nu_i > 0$ and $d\xi > 0 \Rightarrow dn_i > 0$ forward reaction products increase
$\quad d\xi < 0 \Rightarrow dn_i < 0$ reverse reaction products decrease

e.g. i ="reactants" $\nu_i < 0$ and $d\xi > 0 \Rightarrow dn_i < 0$ forward reaction reactants decrease
$\quad d\xi < 0 \Rightarrow dn_i > 0$ reverse reaction reactants increase

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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 $\Delta\mu$

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

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

NOTE: μ_i IS INTENSIVE (J mol⁻¹)
$\Delta\mu_{reaction}$ IS EXTENSIVE (J)

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

$\Delta\mu_{reaction} < 0$ 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)

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

led to

$$\Delta G_{reaction} = \Delta G_{reaction}° + \underline{RT}\ln(Q_P)$$

what about if other species present?

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

$$\Delta\mu_{reaction} = \Delta\mu_{reaction}° + \underline{RT}\ln Q_P$$

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

HANDOUT #45

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

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

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

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

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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)

The word fugacity is derived from the Latin fugere, to flee. In the sense of an "escaping tendency", it was introduced to thermodynamics in 1901 by the American chemist Gilbert N. Lewis.

Fugacity - Wikipedia

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more general μ_i and corrections for non-ideality (~E&R eqn 9.50, p255)$_{4th}$

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

standard conditions

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

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

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

γ_i is activity coefficient, a correction for non-ideality

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

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more general μ_i and corrections for non-ideality

$$\Delta\mu_{reaction} = \Delta\mu^e + \underline{R}T \, ln \, Q$$
where now Q is written in terms of activities

$$Q = \prod_i \left(\frac{a_i}{a_i^\circ}\right)^{\bar{\nu}_i} \qquad Q = \frac{\left(a_C/a_C^0\right)^{\bar{n}_C}\left(a_D/a_D^0\right)^{\bar{n}_D}}{\left(a_A/a_A^0\right)^{\bar{n}_A}\left(a_B/a_B^0\right)^{\bar{n}_B}}$$
unitless

sometimes the $a_i^\circ = 1$ 'unit'
is omitted but rember Q is 'unitless'

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fugacity of gases

1. GASES: $\quad a_i = f_i = \gamma_i \, P_i \leftarrow$ 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

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

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other conventions for activities

2. pure solids and liquids

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

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

so $a_i \approx 1$ for pure solid or liquid
[unless extreme pressure]

EXPERT

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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

WHY CONCENTRATION FOR SOLUTES IN SOLUTION ?
HAVE PROVEN $_iP_i = X_i P_{TOTAL} \Rightarrow Q$ FOR IDEAL GAS.
SOON WILL JUSTIFY $[I] = X_i \Rightarrow Q$ FOR ,SOLUTES IN IDEAL SOLNS.

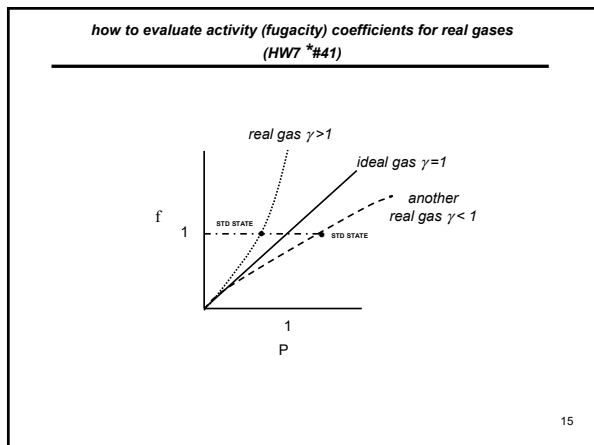activity coefficient γ_i corrects 'ideal' measure of 'concentration

if "activity coefficients unity"

$$a_i = [I] \qquad a_i \equiv f_i = P_i \qquad a_i = 1$$
solute \qquad gas \qquad pure liquid or solid

HW#7 \quad γ=1 \quad except prob. 41* and 43.

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

real gas $\gamma > 1$

ideal gas $\gamma = 1$

another real gas $\gamma < 1$

f

STD STATE

STD STATE

1

P

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how to evaluate activity (fugacity) coefficients for real gases

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

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

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

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

need in a moment

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

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

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

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how to evaluate activity (fugacity) coefficients for real gases

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

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

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

$P_1 \to 0$

$\frac{f(P_i)}{P_i} \to 1$

$\ln\left(\frac{f(P_i)}{P_i}\right) \to 0$

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

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how to evaluate activity (fugacity) coefficients for real gases
(eqn 7.20 E&R$_{4th}$ and HW7 #*41)

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

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

$$z = \frac{\bar{V}_{actual}}{\bar{V}_{ideal}} = \frac{P\bar{V}_{actual}}{RT} \quad (compression\ factor\ E\&R_{4th}\ eqn.\ 7.6)$$

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

$$\gamma(P,T) = exp\left[\int_{P_i \to 0}^{P}\frac{z-1}{P'}dP'\right] \quad (E\&R_{4th}\ eqn\ 7.21)$$

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End of Lecture 17

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activity for solids and liquids ($P_{total} \neq 1$ bar)

$$\mu_i(T) = \mu_i^*(T) + RT\,ln\left(\frac{a_i}{a_i^0}\right)$$

$$\left(\frac{a_i}{a_i^0}\right) = e^{\frac{\mu_i(T)-\mu_i^*(T)}{RT}}$$

$$\left(\frac{\partial\mu_i}{\partial P}\right)_{T,n} = \bar{V}_i$$

$$\mu_i(T,P_{total}) = \mu_i^0(T,1\,bar) + \int_{1bar}^{P_{total}} \bar{V}_i dP \approx \mu_i^0(T,1\,bar) + \bar{V}_i(P_{total}-1\,bar)$$ | HW#6 37 (E&R$_{4th}$ 6.42) |

$$\left(\frac{a_i}{a_i^0}\right)_{l\,or\,s} \approx e^{\frac{\bar{V}_i(P_{total}-1\,bar)}{RT}} \approx 1 \text{ for } P_{total} \text{ near 1 bar (since } \bar{V} \text{ is small for liquids or solids)}$$

for Δμ at high P_{total} would use this in Q for liquids and solids

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