Chemistry 163B, Winter 2014
Lecture 17- Chemical Potential and Activity

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 $\Delta\mu$

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

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

dξ is extent of reaction
dξ > 0 forward reaction
dξ < 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
$dG_{T,P} = 0$ equilibrium

whole pot of mixed reactants and products

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

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

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

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equilibrium in terms of $\Delta\mu$

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

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

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

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

$\Delta\mu_{reaction} < 0$ 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

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

what about if other species present?

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

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

HANDOUT #48

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

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

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

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

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

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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

$a_i^o = 1$ *unit (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

$$Q = \prod_i \underbrace{\left(\frac{a_i}{a_i^{\circ}}\right)^{\nu_i}}_{unitless} \qquad Q = \underbrace{\frac{(a_C)^{\bar{n}_C}(a_D)^{\bar{n}_D}}{(a_A)^{\bar{n}_A}(a_B)^{\bar{n}_B}}}_{\substack{dropped\ the\ a_i^{\circ}=1\ 'unit' \\ but\ Q\ is\ 'unitless'}}$$

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fugacity of gases

1. GASES:

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

partial pressure

fugacity of gas

fugacity coefficient

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

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

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

correction for non-ideality

ideal gas Q_P

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other conventions for activities

2. pure solids and liquids

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

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

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

$[unless\ extreme\ pressure]$

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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

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

activity coefficient γ_i corrects 'ideal' measure of 'concentration

if "activity coefficients unity"

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

HW#8 γ=1 except prob. 41* and 43.

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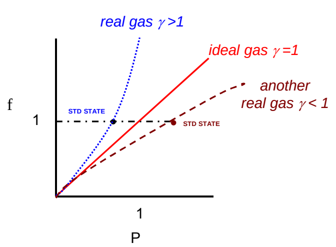
how to evaluate activity (fugacity) coefficients for real gases (HW8 #*41)



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how to evaluate activity (fugacity) coefficients for real gases

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

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

need in a moment

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

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

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

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

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

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

$P_1 \longrightarrow 0$

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

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

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

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how to evaluate activity (fugacity) coefficients for real gases (eqn 7.20 E&R and HW8 #*41)

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

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

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

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

HW8 41*

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

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End of Lecture

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

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

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

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

$$\mu_i(T, P_{total}) = \mu_i^o(T, 1\text{ bar}) + \int_{1bar}^{P_{total}} \bar{V}_i\,dP \approx \mu_i^o(T, 1\text{ bar}) + \bar{V}_i\left(P_{total} - 1\text{ bar}\right)$$

HW#7 37 (E&R 6.5)

$$\left(a_i / a_i^0\right)_{l\text{ or }s} \approx \underbrace{e^{\frac{\bar{V}_i(P_{total} - 1\text{ bar})}{RT}}}_{\text{for }\Delta\mu\text{ at high }P_{total}\text{ would use this in Q for liquids and solids}} \approx 1 \text{ for } P_{total} \text{ near 1 bar (since } \bar{V} \text{ is small for liquids or solids)}$$

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