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 Δμ

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

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

$d\xi$ 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 Δμ

$dG_{T,P} < 0$ spontaneous

$dG_{T,P} = 0$ equilibium

whole pot of mixed reactants and products

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

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

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

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 !!!

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

concentration dependence of μ_i

ideal gas, one component (pure substance)

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

led to

$$\Delta G_{reaction} = \Delta G^{\circ}_{reaction} + RT\, ln(Q_P)$$

what about if other species present?

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

$$\Delta\mu_{reaction} = \Delta\mu^{\circ}_{reaction} + RT\, lnQ_P$$

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

HANDOUT #48

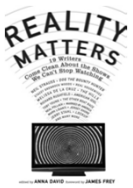
yada -yada- yada: and so forth for $\Delta\mu_{reaction}$

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

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

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

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

$a_i^{\circ} = 1 \quad unit \quad (bar, molar, etc)$

more general μ_i and corrections for non-ideality

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

where now Q is written in terms of activities

$$Q = \prod_i \underbrace{\left(\frac{a_i}{a_i^{\circ}}\right)^{\nu_i}}_{unitless} \qquad Q = \frac{(a_C)^{n_C}(a_D)^{n_D}}{(a_A)^{n_A}(a_B)^{n_B}}$$

dropped the a°=1 'unit' but Q is 'unitless'

fugacity of gases

1. GASES:

$a_i = f_i = \gamma_i P_i$ ← *partial pressure*

fugacity of gas | *fugacity coefficient*

$$Q = \frac{(a_C)^{n_C}(a_D)^{n_D}}{(a_A)^{n_A}(a_B)^{n_B}}$$

$$Q = \frac{\left(\gamma_C \frac{P_C}{1bar}\right)^{n_C}\left(\gamma_D \frac{P_D}{1bar}\right)^{n_D}}{\left(\gamma_A \frac{P_A}{1bar}\right)^{n_A}\left(\gamma_B \frac{P_B}{1bar}\right)^{n_B}}$$

correction for non-ideality

$$Q = \left(\frac{\gamma_C^{n_C}\gamma_D^{n_D}}{\gamma_A^{n_A}\gamma_B^{n_B}}\right)\frac{\left(\frac{P_C}{1bar}\right)^{n_C}\left(\frac{P_D}{1bar}\right)^{n_D}}{\left(\frac{P_A}{1bar}\right)^{n_A}\left(\frac{P_B}{1bar}\right)^{n_B}} = \underline{\gamma}\, Q_P$$

ideal gas Q_P

other conventions for activities

2. pure solids and liquids

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

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

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 $_1P_2=X_1P_{1\,TOTAL}$ ➡ 0 FOR IDEAL GAS. SOON WILL JUSTIFY $[I]=X_i$ ➡ 0 FOR ,SOLUTES IN IDEAL SOLNS.

activity coefficient γ_i corrects 'ideal' measure of 'concentration

if "activity coefficients unity"

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

solute *gas* *pure liquid or solid*

HW#8 γ=1 except prob. 41* and 43.

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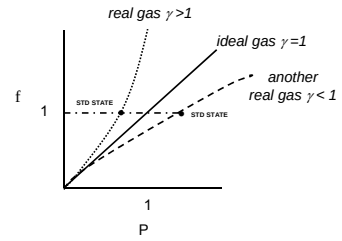
how to evaluate activity (fugacity) coefficients for real gases (HW8 #*41)



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how to evaluate activity (fugacity) coefficients for real gases

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

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

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

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

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

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

$P_1 \longrightarrow 0$

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

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

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

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

$$\ln f(P) = \ln P + \frac{1}{RT}\int_{P_2 \to 0}^{P}\left(\bar{V} - \frac{RT}{P'}\right) dP' = \ln P + \frac{1}{RT}\int_{P_2 \to 0}^{P}(\bar{V}_{ACTUAL} - \bar{V}_{IDEAL\,GAS})\, dP'$$

$$\ln\left(\frac{f(P)}{P}\right) = \ln(\gamma) = \frac{1}{RT}\int_{P_2 \to 0}^{P}\left(\bar{V} - \frac{RT}{P'}\right) dP' = \frac{1}{RT}\int_{P_2 \to 0}^{P}(\bar{V}_{ACTUAL} - \bar{V}_{IDEAL})\, dP'$$

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

$$\ln\gamma = \frac{1}{RT}\int_{P_2 \to 0}^{P} \bar{V}_{ideal}(z-1)dP' = \int_{P_2 \to 0}^{P}\frac{(z-1)}{P'}dP' \qquad \text{HW8 41*}$$

$$\gamma(P,T) = \exp\left[\int_{P_2 \to 0}^{P}\frac{z-1}{P'}dP'\right] \quad (E\ \&\ R\ eqn\ 7.21)$$

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End of Lecture

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

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

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

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

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

HW#7 37 (E&R 6.5)

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

for $\Delta\mu$ at high P_{total} would use this in Q for liquids and solids

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