

1-

$$\mu = \mu^\circ + RT \ln(P/1\text{bar})$$

$$dG = VdP \quad , T = \text{constant}$$

$$\text{ideal gas} \rightarrow PV = nRT \Rightarrow V = \frac{nRT}{P}$$

$$dG = \frac{nRT}{P} dP \rightarrow \frac{dG}{n} = RT \frac{dP}{P} \rightarrow \frac{dG}{n} = \bar{G} = \mu$$

$$\rightarrow \int \mu = RT \int \frac{dP}{P} \Rightarrow \mu - \mu^\circ = RT \ln \frac{P}{P^\circ}$$

$$P^\circ = 1\text{bar} \Rightarrow \mu = \mu^\circ + RT \ln(P/1\text{bar})$$

$$2- \mu_i(l) = \mu_i^*(l) + RT \ln \left(\frac{P_i}{P_i^*} \right)$$

$$\mu_i^*(l) = \mu_i^*(g)$$

$$\mu_i^*(l) = \mu_i^*(g) = \mu_i^*(g) + RT \ln \frac{P_i^*}{1 \text{ bar}}$$

$$\text{same} \rightarrow \mu_i(l) = \mu_i(g) = \mu_i^*(g) + RT \ln \frac{P_i}{1 \text{ bar}}$$

the standard chemical potential of component 1 (solvent) is the same in the pure state and in the solution $\Rightarrow \mu_i(g) = \mu_i^*(g)$ & $\mu_i(g) = \mu_i^*(l) - RT \ln(P_i^*/1 \text{ bar})$

$$\begin{aligned} \Rightarrow \mu_i(l) &= \mu_i^*(g) + RT \ln \left(\frac{P_i}{1 \text{ bar}} \right) \\ &= \mu_i^*(l) - RT \ln \frac{P_i^*}{1 \text{ bar}} + RT \ln \frac{P_i}{1 \text{ bar}} \\ &= \mu_i^*(l) + RT \ln \left(\frac{P_i}{P_i^*} \right) \textcircled{1} \end{aligned}$$

for non-ideal solution we have:

$$\mu_i(l) = \mu_i^*(l) + RT \ln a_i \textcircled{2} \rightarrow \text{activity}$$

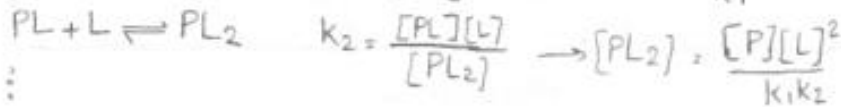
a = activity is related to concentration (mole fraction):

$$a_i = \gamma_i x_i$$

$$\textcircled{1} \approx \textcircled{2} \Rightarrow a = \frac{P_i}{P_i^*}$$

3.

$$\frac{Y}{[L]} = \frac{n}{K} - \frac{Y}{K}$$



$$Y = \frac{\text{concentration of } L \text{ bound to } P}{\text{total concentration of all forms of } P}$$

$$Y = \frac{[PL] + 2[PL_2] + \dots + n[PL_n]}{[P] + [PL] + [PL_2] + \dots + [PL_n]}$$

$$Y = \frac{\frac{[P][L]}{K_1} + 2\frac{[P][L]^2}{K_1 K_2} + \dots + n\frac{[P][L]^n}{K_1 K_2 \dots K_n}}{[P] + \frac{[P][L]}{K_1} + \frac{[P][L]^2}{K_1 K_2} + \dots + \frac{[P][L]^n}{K_1 K_2 \dots K_n}}$$

$$Y = \frac{[L]/K_1 + 2[L]^2/K_1 K_2 + \dots + n[L]^n/K_1 K_2 \dots K_n}{1 + [L]/K_1 + [L]^2/K_1 K_2 + \dots + [L]^n/K_1 K_2 \dots K_n}$$

$$K = \sqrt{K_1 K_2 \dots K_n}$$

$$Y = \frac{2[L]/K + 2[L]^2/K^2 + \dots + n[L]^n/K^n}{1 + 2[L]/K + [L]^2/K^2 + \dots + [L]^n/K^n}$$

$$Y = \frac{n[L]/K (1 + [L]/K)^{n-1}}{(1 + [L]/K)^n} = \frac{n[L]}{[L] + K}$$

$$Y[L] + YK = n[L]$$

$$\frac{Y[L]}{K} + Y = \frac{n[L]}{K}$$

$$Y = \frac{n[L]}{K} - \frac{Y[L]}{K}$$

$$\frac{Y}{[L]} = \frac{n}{K} - \frac{Y}{K}$$

4-

$$\ln \frac{K_2}{K_1} = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{1.571}{0.534} = \frac{\Delta_r H^\circ}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{960 \text{ K}} - \frac{1}{1260 \text{ K}} \right)$$

$$\Delta_r H^\circ = 3.62 \times 10^4 \text{ J mol}^{-1}$$

5-

Using the standard molar Gibbs energy of formation for the reactants and products, calculate $\Delta_r G^\circ$ for the reaction at 25° C, from which the equilibrium constant at 25° C is obtained.

$$\begin{aligned}\Delta_r G^\circ &= 2\Delta_f \bar{G}^\circ [\text{NO}(g)] - \Delta_f \bar{G}^\circ [\text{N}_2(g)] - \Delta_f \bar{G}^\circ [\text{O}_2(g)] \\ &= 2(86.7 \text{ kJ mol}^{-1}) - 0 \text{ kJ mol}^{-1} - 0 \text{ kJ mol}^{-1} \\ &= 173.4 \text{ kJ mol}^{-1}\end{aligned}$$

Since $\Delta_r G^\circ = -RT \ln K$,

$$\begin{aligned}\ln K &= -\frac{\Delta_r G^\circ}{RT} = -\frac{173.4 \times 10^3 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.2 \text{ K})} = -69.940 \\ K &= 4.221 \times 10^{-31} = 4.22 \times 10^{-31}\end{aligned}$$

The equilibrium constant at 1500 K can be calculated using the van't Hoff equation once $\Delta_r H^\circ$ for the reaction is known.

$$\begin{aligned}\Delta_r H^\circ &= 2\Delta_f \bar{H}^\circ [\text{NO}(g)] - \Delta_f \bar{H}^\circ [\text{N}_2(g)] - \Delta_f \bar{H}^\circ [\text{O}_2(g)] \\ &= 2(90.4 \text{ kJ mol}^{-1}) - 0 \text{ kJ mol}^{-1} - 0 \text{ kJ mol}^{-1} \\ &= 180.8 \text{ kJ mol}^{-1}\end{aligned}$$

Apply the van't Hoff equation, assuming $\Delta_r H^\circ$ is temperature independent.

$$\begin{aligned}\ln \frac{K_2}{K_1} &= \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ \ln \frac{K_2}{4.221 \times 10^{-31}} &= \frac{180.8 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{298.2 \text{ K}} - \frac{1}{1773.2 \text{ K}} \right) \\ K_2 &= 9.34 \times 10^{-5}\end{aligned}$$

6-

For the reaction $\text{cis-2-butene}(g) \rightleftharpoons \text{trans-2-butene}(g)$,

$$\begin{aligned}\Delta_r G^\circ &= \Delta_f \bar{G}^\circ [\text{trans-2-butene}] - \Delta_f \bar{G}^\circ [\text{cis-2-butene}] \\ &= 64.10 \text{ kJ mol}^{-1} - 67.15 \text{ kJ mol}^{-1} \\ &= -3.05 \text{ kJ mol}^{-1}\end{aligned}$$

Since

$$K_P = \frac{P_{\text{trans-2-butene}}}{P_{\text{cis-2-butene}}}$$

The equilibrium constant gives the ratio of equilibrium pressures of the isomers. This ratio can be determined using $\Delta_r G^\circ$.

$$\ln K_P = -\frac{\Delta_r G^\circ}{RT} = -\frac{-3.05 \times 10^3 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 1.231$$

$$K_P = \frac{P_{\text{trans-2-butene}}}{P_{\text{cis-2-butene}}} = 3.42$$

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$$\begin{aligned}\Delta_r G &= \Delta_r G^\circ + RT \ln Q = \Delta_r G^\circ + RT \ln \frac{[\text{glucose-6-phosphate}]}{[\text{glucose}][\text{HPO}_4^{2-}]} \\ &= 13.4 \times 10^3 \text{ J mol}^{-1} + (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(310 \text{ K}) \ln \frac{1.6 \times 10^{-4}}{(4.5 \times 10^{-2})(2.7 \times 10^{-3})} \\ &= 14.1 \times 10^3 \text{ J mol}^{-1} > 0\end{aligned}$$

Therefore, the reaction is not spontaneous.

The dissociation constant can be obtained by plotting $Y/[L]$ vs Y . The slope is $-1/K_d$.

L and Y are obtained using the following relations:

$$[L] = [\text{Ca}^{2+}]_{\text{total}} - [\text{Ca}^{2+}]_{\text{bound}}$$

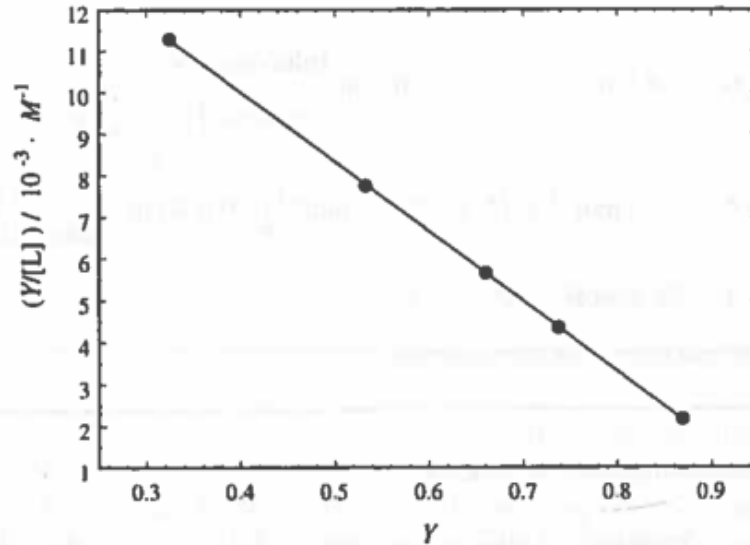
$$Y = \frac{[\text{Ca}^{2+}]_{\text{bound}}}{96 \mu\text{M}}$$

According to the data given above, the values of $[L]$, Y , and $Y/[L]$ are

| | | | | | |
|---------------------------------------|--------|--------|--------|--------|--------|
| $[L]/\mu\text{M}$ | 28.8 | 68.8 | 116.6 | 169.2 | 396.6 |
| Y | 0.3250 | 0.5333 | 0.6604 | 0.7375 | 0.8688 |
| $(Y/[L])/10^{-3} \cdot \text{M}^{-1}$ | 11.28 | 7.751 | 5.664 | 4.359 | 2.191 |

The slope of the plot is -16.72×10^{-3} . Therefore,

$$K_d = \frac{1}{16.72 \times 10^{-3}} = 59.8$$



As discussed in the text for the decomposition of calcium carbonate, a reaction favors the formation of products at equilibrium when

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ < 0$$

$\Delta_r H^\circ$ and $\Delta_r S^\circ$ are

$$\begin{aligned} \Delta_r H^\circ &= \Delta_f \bar{H}^\circ [\text{MgO}(s)] + \Delta_f \bar{H}^\circ [\text{CO}_2(g)] - \Delta_f \bar{H}^\circ [\text{MgCO}_3(s)] \\ &= -601.8 \text{ kJ mol}^{-1} + (-393.5 \text{ kJ mol}^{-1}) - (-1095.8 \text{ kJ mol}^{-1}) \\ &= 100.5 \text{ kJ mol}^{-1} \\ \Delta_r S^\circ &= \bar{S}^\circ [\text{MgO}(s)] + \bar{S}^\circ [\text{CO}_2(g)] - \bar{S}^\circ [\text{MgCO}_3(s)] \\ &= 26.78 \text{ J K}^{-1} \text{ mol}^{-1} + 213.6 \text{ J K}^{-1} \text{ mol}^{-1} - 65.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 174.68 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Therefore, for the reaction to begin to favor products,

$$\begin{aligned} \Delta_r H^\circ - T \Delta_r S^\circ &= 100.5 \times 10^3 \text{ J mol}^{-1} - T (174.68 \text{ J K}^{-1} \text{ mol}^{-1}) < 0 \\ T &> \frac{100.5 \times 10^3 \text{ J mol}^{-1}}{174.68 \text{ J K}^{-1} \text{ mol}^{-1}} \\ T &> 575.3 \text{ K} \end{aligned}$$

$\Delta_r G^{o'}$ is calculated from the standard molar Gibbs energies of formation of the reactants and products.

$$\begin{aligned}\Delta_r G^{o'} &= \Delta_f \bar{G}^o (\text{glycylglycine}) + \Delta_f \bar{G}^o (\text{H}_2\text{O}) - 2\Delta_f \bar{G}^o (\text{glycine}) \\ &= (-493.1 \text{ kJ mol}^{-1}) + (-237.2 \text{ kJ mol}^{-1}) - 2(-379.9 \text{ kJ mol}^{-1}) \\ &= 29.5 \text{ kJ mol}^{-1}\end{aligned}$$

The equilibrium constant can now be determined.

$$\begin{aligned}\ln K' &= -\frac{\Delta_r G^{o'}}{RT} = -\frac{29.5 \times 10^3 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = -11.91 \\ K' &= 6.72 \times 10^{-6}\end{aligned}$$

If $\Delta_r G^{o'}$ at 310 K is essentially the same as that at 298 K, then K' at 310 K is also approximately the same as that at 298 K. The small K' indicates that the formation of a dipeptide (and hence a protein molecule) is not a spontaneous process under standard-state conditions. Protein synthesis *in vivo* is carried out both under other conditions and with the aid of ATP.

First calculate the average molar mass of the mixture, \mathcal{M}_{mix} , assuming the mixture behaves ideally. Since

$$P = \frac{n_{\text{mix}}RT}{V} = \frac{m_{\text{mix}}RT}{\mathcal{M}_{\text{mix}}V} = \frac{m_{\text{mix}}}{V} \frac{RT}{\mathcal{M}_{\text{mix}}} = \frac{\rho_{\text{mix}}RT}{\mathcal{M}_{\text{mix}}}$$

the average molar mass is

$$\mathcal{M}_{\text{mix}} = \frac{\rho_{\text{mix}}RT}{P} = \frac{(2.3 \text{ g L}^{-1})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(347 \text{ K})}{1.3 \text{ atm}} = 50.4 \text{ g mol}^{-1}$$

The average molar mass is also related to the mole fractions of the components and their molar masses:

$$\begin{aligned} x_{\text{NO}_2}\mathcal{M}_{\text{NO}_2} + x_{\text{N}_2\text{O}_4}\mathcal{M}_{\text{N}_2\text{O}_4} &= 50.4 \text{ g mol}^{-1} \\ x_{\text{NO}_2}(46.01 \text{ g mol}^{-1}) + x_{\text{N}_2\text{O}_4}(92.02 \text{ g mol}^{-1}) &= 50.4 \text{ g mol}^{-1} \end{aligned}$$

Since $x_{\text{N}_2\text{O}_4} = 1 - x_{\text{NO}_2}$, the above equation contains only 1 unknown and can be readily solved.

$$\begin{aligned} x_{\text{NO}_2}(46.01 \text{ g mol}^{-1}) + (1 - x_{\text{NO}_2})(92.02 \text{ g mol}^{-1}) &= 50.4 \text{ g mol}^{-1} \\ 46.01x_{\text{NO}_2} + 92.02 - 92.02x_{\text{NO}_2} &= 50.4 \\ 46.01x_{\text{NO}_2} &= 41.62 \\ x_{\text{NO}_2} &= 0.905 \\ x_{\text{N}_2\text{O}_4} &= 1 - 0.905 = 0.095 \end{aligned}$$

The partial pressures of the gases are

$$\begin{aligned} P_{\text{NO}_2} &= x_{\text{NO}_2}P = (0.905)(1.3 \text{ atm}) = 1.18 \text{ atm} = 1.2 \text{ atm} \\ P_{\text{N}_2\text{O}_4} &= P - P_{\text{NO}_2} = 1.3 \text{ atm} - 1.18 \text{ atm} = 0.12 \text{ atm} = 0.1 \text{ atm} \end{aligned}$$

The equilibrium constant for the dissociation reaction, $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, is

$$K_P = \frac{(P_{\text{NO}_2}/P^\circ)^2}{P_{\text{N}_2\text{O}_4}/P^\circ} = \frac{[(1.18 \text{ atm}) \left(\frac{1.013 \text{ bar}}{1 \text{ atm}}\right) / 1 \text{ bar}]^2}{(0.12 \text{ atm}) \left(\frac{1.013 \text{ bar}}{1 \text{ atm}}\right) / 1 \text{ bar}} = 12$$

12-

12-



$$n(1-\alpha) \quad 2n\alpha$$

α = the fraction of the A molecules dissociated
 n = the number of moles of A originally present
 $n(1+\alpha)$ = total number of moles of molecules at equilibrium

$$\Rightarrow \underset{\substack{\text{mole fraction} \\ \text{of A}}}{x_A} = \frac{n(1-\alpha)}{n(1+\alpha)} = \frac{1-\alpha}{1+\alpha} \quad \Rightarrow P_A = \left(\frac{1-\alpha}{1+\alpha}\right)P$$

$$x_B = \frac{2n\alpha}{n(1+\alpha)} = \frac{2\alpha}{1+\alpha} \quad \Rightarrow P_B = \left(\frac{2\alpha}{1+\alpha}\right)P$$

$$\underset{\substack{\text{total} \\ \text{pressure of sys.}}}{K_P} = \frac{P_B^2}{P_A} = \frac{\left(\frac{2\alpha}{1+\alpha}P\right)^2}{\left(\frac{1-\alpha}{1+\alpha}P\right)} = \left(\frac{4\alpha^2}{1-\alpha^2}\right)P$$

$$\Rightarrow \alpha = \sqrt{\frac{K_P}{K_P + 4P}}$$

$\left(\frac{\partial K_P}{\partial P}\right)_T = 0 \rightsquigarrow$ for ideal gas in equilibrium

$$\xrightarrow[\text{remain constant}]{\text{by increasing } P, K_P} \downarrow \alpha = \sqrt{\frac{K_P \downarrow \text{constant}}{K_P + 4P \uparrow}} \Rightarrow \alpha \downarrow$$

$\Rightarrow \uparrow x_A = \frac{(1-\alpha \downarrow) \uparrow}{(1+\alpha \downarrow) \downarrow} \Rightarrow$ The ratio of nominator to denominator is increasing so x_A is rising up.