

CONCENTRATION and FREE ENERGY

ΔG_{rx}° can be obtained from:

a) ΔG_f° values (App. C) ← only good at 298K

b) $\Delta G_{rx}^{\circ} = \Delta H_{rx}^{\circ} - T \Delta S_{rx}^{\circ}$ ← get ΔG_{rx}° at any T

We have a problem, however. We rarely have standard conditions (1 atm, 1 M). Much, much more useful if we have an expression that we can use with any concns.

For any rx, reacts → prods, the sign of ΔG_{rx} tells us if we are going forward, backward or at equilibrium.

$\Delta G_{rx} -ve$	$\xrightarrow{\text{Rx}}$
$\Delta G_{rx} = 0$	equilib.
$\Delta G_{rx} +ve$	$\xleftarrow{\text{Rx}}$

Hence ΔG_{rx} must depend on concns of reacts and products

Sec 14.5 9 Ed.
 p 595
 Sec 15.5
 p 632 8 Ed.

You (sort of!) already know this.
 Think about Q , the reaction quotient.

Remember, for a rx. with concns/P's any values,

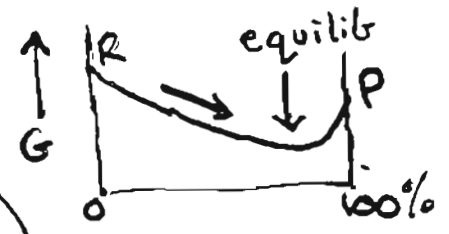


$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{or} \quad Q_p = \frac{P_c^c \cdot P_d^d}{P_A^a \cdot P_B^b}$$

Units: molarity (solns) atm (gases)

Note - for pure solids/liqs, $[] = 1$

Let's say the rx. is heading toward equilibrium where $Q = K$ (equilib. const.)



If $Q < K$, the rx. wants to go forward, increasing $[C]$ and $[D]$ and decreasing $[A]$ and $[B]$ until $Q = K$ (at equilib.)

So, we can write

$$\Delta G_{rx} = \Delta G_{rx}^{\circ} + RT \ln Q$$

see prev. page to get these
 ↑
 std. conditions value (unit concns)
 ↑
 a fixed value at a given T

↑↑
 additional term to account for non-unit concns

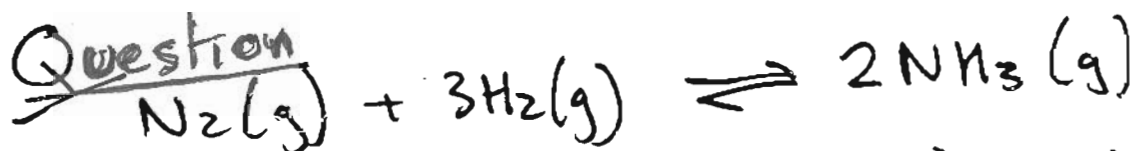
The $RT \ln Q$ term (which depends on $\frac{[prods]}{[reacts]}$) can add or subtract to the std. value ΔG_{rx}° .

• $Q < 1$, $RT \ln Q$ is -ve; ΔG_{rx} is more -ve than ΔG°

• $Q > 1$, ——— " ——— +ve. ——— " ——— +ve than ΔG°

Note: If all concns/ $P_i = 1$, $RT \ln Q = 0$ and $\Delta G_{rx} = \Delta G_{rx}^\circ$ } std. state conditions

Question



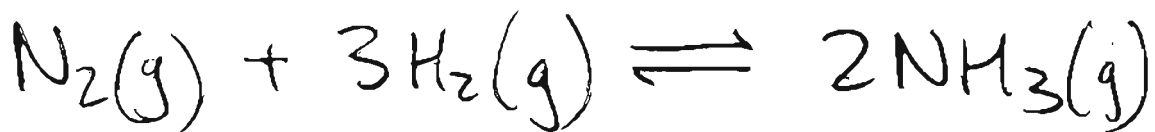
At 298, the partial pressures in a rx. mixture are $P_{N_2} = 0.25 \text{ atm}$, $P_{H_2} = 0.55 \text{ atm}$ and $P_{NH_3} = 0.95 \text{ atm}$. Calculate ΔG_{rx} .

$$\Delta G_{rx} = -33.28 \text{ kJ} + \underbrace{(8.314)}_{\substack{\text{J K}^{-1} \text{ mol}^{-1} \\ \uparrow \\ \Delta G_{rx}^\circ \text{ using tables} \\ \text{of } \Delta G_f^\circ \text{ data}}} (298) \ln \underbrace{\frac{(0.95)^2}{(0.25)(0.55)^3}}_Q$$

$$\Delta G_{rx} = \underline{\underline{-25.7 \text{ kJ}}}$$

ΔG_{rx} is -ve; \therefore rx. is spont. in forward direction. An increase in NH_3 will continue until Q becomes = K (the equilibrium constant) and hence $\Delta G_{rx} = 0$ i.e. equilibrium.

(19)



$$\Delta G_{\text{rxn}} = \Delta G^\circ + RT \ln Q \quad \left. \vphantom{\Delta G_{\text{rxn}}} \right\} = \frac{Q}{P_{\text{N}_2} \times P_{\text{H}_2}^3} = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \times P_{\text{H}_2}^3}$$

$$= -33.28 + 2.478 \ln Q$$

Expt.	reacts.		prod.	Q	RT ln Q	$\Delta G, \text{kJ}$
	P_{N_2}	P_{H_2}	P_{NH_3}			
A	1	1	0	0	$-\infty$	$-\infty$
B	1	1	0.001	10^{-6}	-34.24	-67.52
C	1	1	0.1	10^{-2}	-11.64	-44.92
D	1	1	1	1	0	-33.28
E	1	1	100	10^4	+22.83	-10.45
F	1	1	825	6.8×10^5	+33.28	0.0
G	1.47	0.01	1	6.8×10^5	+33.28	0.0
H	0.01	0.1	2.61	6.8×10^5	+33.28	0.0
I	0.01	0.1	26.1	6.8×10^7	+44.77	+11.49
J	0.01	0.01	100	10^{12}	+68.48	+35.2
K	0	1	1	∞	$+\infty$	$+\infty$

$= K_{\text{eq}}$

ΔG_{rx} and K_{eq} .

$$\Delta G_{rx} = \Delta G_{rx}^{\circ} + RT \ln Q$$

At equilibrium, all concns (or P's) are equilibrium concns (or P's)

- hence $Q = K$

and, of course, $\Delta G_{rx} = 0$

$$\therefore 0 = \Delta G_{rx}^{\circ} + RT \ln K$$

$$\boxed{\Delta G_{rx}^{\circ} = -RT \ln K}$$

$$K_{eq} = e^{-\frac{\Delta G^{\circ}}{RT}} \quad \text{or} \quad K_{eq} = 10^{-\frac{\Delta G^{\circ}}{2.303 RT}}$$

Every rx. has a definite ΔG° and a definite K_{eq} at a particular temp.

For $K > 1$, $\ln K$ is +ve,

and ΔG° is -ve (\therefore rx $L \rightarrow R$)

For $K < 1$, $\ln K$ is -ve,

and ΔG° is +ve (\therefore rx $L \leftarrow R$).

Link between ΔG_{rx} and Q (quotient)

$$\Delta G_{rx} = \Delta G_{rx}^{\circ} + RT \ln Q$$

$$\text{and } \Delta G_{rx}^{\circ} = -RT \ln K$$

$$\therefore \Delta G_{rx} = -RT \ln K + RT \ln Q$$

$$\text{Hence } \Delta G_{rx} = RT \ln \frac{Q}{K}$$

Note. i.e. concns = 1M
P's = 1atm

① Under standard conditions, $Q = 1$

$$\Delta G_{rx} = \Delta G_{rx}^{\circ} = -RT \ln K$$

② At equilibrium, $Q = K$

$$\Delta G_{rx} = 0$$

③ If $Q < K$ (i.e. if $\frac{Q}{K} < 1$)

ΔG -ve. Rx. goes $L \rightarrow R$ until $Q = K$

④ If $Q > K$ (i.e. if $\frac{Q}{K} > 1$)

ΔG +ve. Rx. goes $L \leftarrow R$ until $Q = K$

Q The equilibrium constant for the rx,
 $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
is $1.75 \times 10^{-5} \text{ M}$ at 25°C .

a) Calculate $\Delta G_{\text{rx}}^\circ$ at 25°

b) Will $\text{NH}_3(\text{g})$ react with water when both
 $[\text{NH}_4^+]$ and $[\text{OH}^-] = 1.0 \times 10^{-6} \text{ M}$ and
 $[\text{NH}_3] = 0.050 \text{ M}$?

$$\text{a) } \Delta G_{\text{rx}}^\circ = -RT \ln K = -8.314(298) \ln 1.75 \times 10^{-5} \\ = + \underline{27.1 \text{ kJ mol}^{-1}}$$

i.e. Under std. conditions (unit concs), the
rx goes from $\text{L} \leftarrow \text{R}$

b) Under non-standard conditions

$$\Delta G_{\text{rx}} = \Delta G_{\text{rx}}^\circ + RT \ln Q$$

$$Q = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][\text{H}_2\text{O}]} = \frac{[1.0 \times 10^{-6}]^2}{5.0 \times 10^{-2}} = 2.0 \times 10^{-11} \text{ M}$$

$$\Delta G_{\text{rx}} = +27.1 + 8.314 \times 10^{-3}(298) \ln 2.0 \times 10^{-11} \\ = - \underline{33.9 \text{ kJ mol}^{-1}}$$

Hence NH_3 will react with $\text{H}_2\text{O} \Rightarrow$ more NH_4^+ and OH^-

Note that $Q < K$ (i.e. rx. wants to go forward)

Temperature and the Equilib. Constant K

$$\Delta G_{rx}^{\circ} = \Delta H_{rx}^{\circ} - T \Delta S_{rx}^{\circ} \quad (\text{eq. y})$$

ΔG_{rx}° depends on T

We'll assume that ΔH° and ΔS° do not

$$\Delta G_{rx}^{\circ} = -RT \ln K \quad (\text{eq. z})$$

\uparrow depends on T \uparrow also dep. on T.

Combining equations y and z.

$$\ln K = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$

A plot of $\ln K$ vs $\frac{1}{T}$ gives a straight line of slope $-\frac{\Delta H^{\circ}}{R}$
 \uparrow assuming $\Delta H^{\circ}, \Delta S^{\circ}$ indep. of T.

