

$$\Delta G = \Delta G^0 + RT \ln (Q/Q_0)$$

what are the WORDS?

“ ΔG is ΔG when all concentrations are 1 and ideal, plus a correction for actual concentrations, $RT \ln(Q/Q_0)$ ”

At equilibrium: $\Delta G = 0$; so $\Delta G^0 = -RT \ln (Q_{eq}/Q_0)$
which is the same as $\Delta G^0 = -RT 2.3 \log (Q_{eq}/Q_0)$
 $\Delta G^0 = -2.3RT \log (Q_{eq}/Q_0)$

At 298 K: $\Delta G^0 = - (2.3)(8.3145)(298) \log (Q_{eq}/Q_0)$
 $-5700 \log (Q_{eq}/Q_0)$ in J
 $-5.7 \log (Q_{eq}/Q_0)$ in kJ

$Q_{eq}/Q_0 = K/1 = K$, the equilibrium constant

Therefore: $\Delta G^0 = -5.7 \log (K)$

$$\Delta G^0 = -2.3RT \log (Q_{eq}/Q_0) = -5.7 \log (K)$$

$$K = ? \quad = 10^{-\Delta G^0/5.7}$$

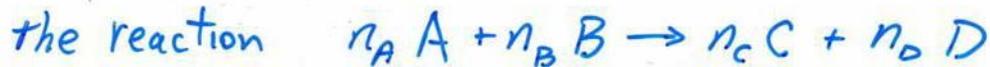
<u>ΔG^0</u>	$K = 10^{-\Delta G^0/5.7}$ at 298K and <u>IDEAL</u>
+17.1	$10^{-3} = 0.001$
+11.4	$10^{-2} = 0.01$
+ 5.7	$10^{-1} = 0.1$
0.0	$10^{-0} = 1.0$
- 5.7	$10^{+1} = 10$
- 11.4	$10^{+2} = 100$
- 17.1	$10^{+3} = 1000$

what if NOT Ideal??

THE REAL Q

recall: $\Delta G = \Delta G^\circ + RT \ln\left(\frac{Q}{Q^\circ}\right)$ always

FOR IDEAL gases & solutions:



Q_{Ideal}

$$\frac{C_C^{n_C} C_D^{n_D}}{C_A^{n_A} C_B^{n_B}}$$

$\gamma = \text{activity coef.}$
 $\gamma C = \text{activity} = a$

$$Q_{\text{Real}} = \frac{a_C^{n_C} a_D^{n_D}}{a_A^{n_A} a_B^{n_B}} = \frac{(\gamma_C C_C)^{n_C} (\gamma_D C_D)^{n_D}}{(\gamma_A C_A^{n_A}) (\gamma_B C_B^{n_B})}$$

IF $\gamma_A < 1$ \bar{G}_A i.e., μ_A is more neg.
than expected from conc.
i.e. more stable

IF $\gamma_A > 1$ μ_A is less stable

STANDARD STATE: $C = 1$ $\gamma = 1$

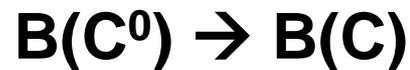
so $Q^\circ = 1$ (in this course.)

Activity = $a = \gamma C$

where C = concentration

and γ = activity coefficient

Consider the “reaction” of changing the concentration of **substance B** from standard state, C^0 , to any concentration C ,



IDEAL: $\Delta G = \Delta H - T\Delta S$

$$= 0 + RT \ln \frac{C}{C^0}$$

REAL:

$$\Delta G = \Delta H + RT \ln \frac{C}{C^0}$$

Due to interactions

Now, do several steps of NOTHING

$$\Delta H = RT \frac{\Delta H}{RT}$$

$$\Delta H = RT \ln\left(e^{\frac{\Delta H}{RT}}\right)$$

$$= RT \ln \gamma$$

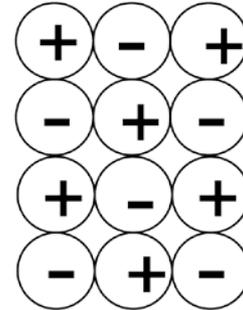
$$\gamma = e^{\frac{\Delta H}{RT}} \quad \text{by definition for convenience}$$

$$\begin{aligned} \therefore \Delta G &= RT \ln \gamma + RT \ln \frac{c}{c^0} \\ &= RT \ln \frac{\gamma c}{c^0} = RT \ln \frac{a}{c^0} \end{aligned}$$

Activity coefficient of ions in solution:

is about ion atmospheres:

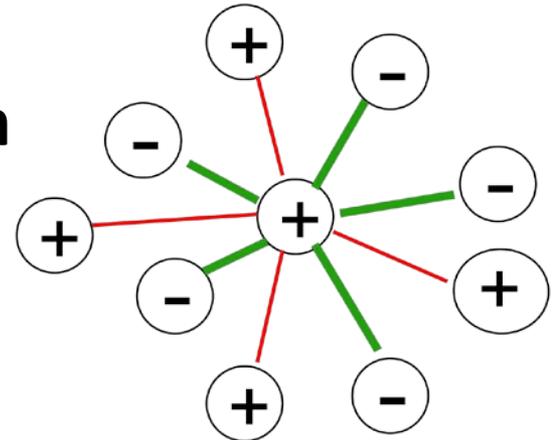
crystal: perfect correlation



Real solution: good correlation

strong negative terms

weak positive terms



Net **negative** ΔG interaction

TABLE 23-4 Mean-activity coefficients for electrolytes in water at 25°C*

Molality	0.001	0.005	0.01	0.05	0.10	0.50	1.00	2.00
Debye-Hückel theory for $AB \rightarrow A^+ + B^-$	0.965	0.920	0.890	0.770				
HCl	0.965	0.929	0.905	0.830	0.794	0.757	0.809	1.009
NaCl	0.965	0.927	0.902	0.819	0.778	0.681	0.657	0.668
Debye-Hückel theory for $AB \rightleftharpoons A^{++} + B^{=}$	0.744	0.515						
ZnSO ₄	0.700	0.477	0.387	0.202	(0.150)	0.063	0.043	0.035
CdSO ₄	0.697	0.476	0.383	0.199	(0.150)	0.061	0.041	0.032

*Data are from H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, 1950; and B. E. Conway, "Electrochemical Data," Elsevier Publishing Company, Amsterdam, 1962.

08: 19-7

Example using activities:



Suppose $\Delta G^\circ = +11.4 \frac{kJ}{mol} = 2 \times 5.7$

$$K_a = 10^{-2} \quad (\text{at } 298 \text{ K})$$

If assume IDEAL at $[HA] = 1 \text{ M}$

$$K_a = \frac{[H^+][A^-]}{[HA]} = 0.01$$

$$[H^+] = [A^-] = 0.1 \text{ M at equil.}$$

But attraction of H^+ & A^- at 0.1 M
makes them MORE stable

$$\gamma \cong 0.5 \quad \text{for both } H^+ \text{ \& } A^-$$

$$\gamma_{HA} \cong 1$$

$$\text{So: } K = \frac{a_{H^+} a_{A^-}}{1} = a^2 = 0.01$$

$$a = \gamma c = (0.5)c = 0.1$$

$$c_{eq} = 0.2 \text{ M for } H^+ \text{ \& } A^-$$

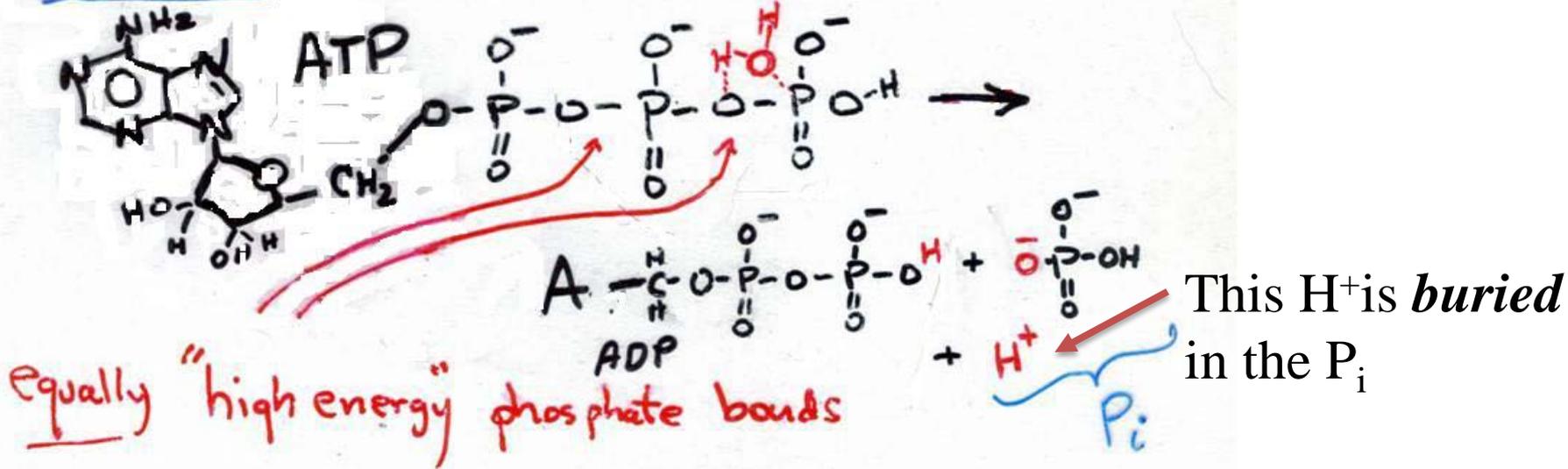
Electrostatic attraction makes ΔG more negative; The reaction **goes further right than expected** from ideal behavior. Actual concentration is 0.2 M for each ion.

$\gamma=0.5$ is like saying the concentrations of H^+ and A^- are less. LeChatelier says this will shift the equilibrium to the right.

Importance of the "Biochemical Standard State"

Hydrolysis of diphosphate bond.

29



$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = -21,000\text{J} - 298(-100\text{ J/K}) \\ &= -21 + 30 \\ &= +9\text{ kJ/mol} \end{aligned}$$

!!!??? Really?

But ΔG° means $[H^+] = 1$ pH = 0
Biological Standard State: $[H^+] = 10^{-7}$; others as usual.

Let's *SEPARATE* the **H⁺** from the **P_i**



What does LeChatelier say if we are at *pH 7* ?

$$\Delta G = \Delta G^0 + RT \ln \frac{Q}{Q^0} = +9 + RT \ln \frac{[\text{ADP}][\text{H}^+][\text{P}_i]}{[\text{ATP}][\text{X}_{\text{H}_2\text{O}}]}$$

Use biological standard state = pH 7

$$\Delta G = \Delta G^{0'} + RT \ln \frac{Q}{Q^{0'}} = -31 + RT \ln \frac{[\text{ADP}][\text{H}^+][\text{P}_i]}{[\text{ATP}][\text{X}_{\text{H}_2\text{O}}]}$$

$$\frac{(1)(1 \times 10^{-7})}{(1)(1)}$$

$$\Delta G^{0'} = \Delta G^0 + RT \ln \frac{Q^{0'}}{Q^0} = \Delta G^0 + RT \ln \frac{(1)(1 \times 10^{-7})}{(1)(1)}$$

$$\frac{(1)(1)}{(1)(1)(1)}$$

$$\frac{(1)(1)}{(1)(1)}$$

$$= +9 + 5.7 \times (-7) = +9 - 39.9 = -31$$

$$Q^{0'} = \frac{[\text{ADP}][\text{H}^+][\text{P}_i]}{[\text{ATP}][\text{X}_{\text{H}_2\text{O}}]} = \frac{(1)(1 \times 10^{-7})}{(1)(1)} = 1 \times 10^{-7}$$

The famed “high energy phosphate bond” yields little more free energy than a hydrogen bond!

What is K when $\Delta G^{0'} = -31 \text{ kJ/mol}$?

$$K = 10^{\Delta G^{0'}/5.7} = 10^{-31/5.7} = 2.7 \times 10^5$$

i.e., enough but not too much.

How does K_{equil} depend on temperature?

LeChatlier:

adding heat (raising temperature) shifts equilibrium (changes K) in the direction that uses the heat (lowers temperature).

Endothermic ($\Delta H = +$) absorbs heat;
rxn will therefore use heat and lower the T , i.e.,
will shift to the right (K increases with rising T)

Exothermic ($\Delta H = \text{negative}$) gives off heat
and raise the T ;
therefore shift to the left (K decreases with rising T)

Saying the same thing with ΔG°

EFFECT OF TEMPERATURE ON K

$$\Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ$$

$$\ln K_2 = -\frac{\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R}$$

$$\ln K_1 = -\frac{\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R}$$

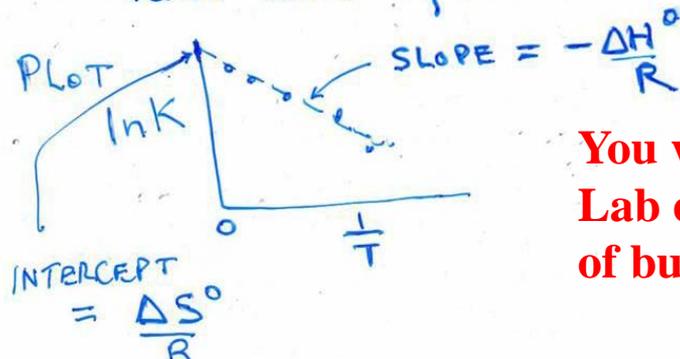
divide by $-RT$ and call it T_2
do same for T_1

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

Subtract
assuming ΔH°
& ΔS° const.

$$= \ln \frac{K_2}{K_1}$$

Van't Hoff equation (one of several)



**You will do this for the
Lab experiment on the dissolving
of butanol in water.**