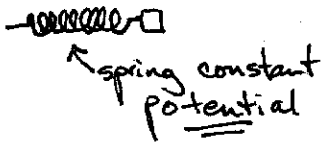
10/4/99

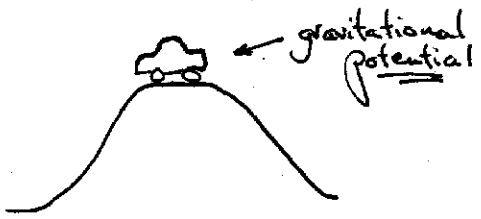
We'll derive a common expression

Chapter 4 — Use what we've learned

— Shift towards ΔG as the "energy of choice" to indicate "spontaneity".
→ <u>Can</u> a reaction go forward?
Remember: thermo does <u>not</u> tell us about <u>kinetics</u>.

In Chapter 3 (p. 89), when introducing <u>G</u>, we noted that the <u>chemical potential</u>, μ, is approximated by G.





We'll be interested in <u>energy levels</u>.
Each "molecular arrangement" is called a microscopic state.
Different states may have different or the same (degenerate) energies.

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

Spontaneity is a drive towards
lower enthalpy
AND
higher entropy
} NET is key.

Le Chatelier

$$A + B \rightleftharpoons C + D$$

Increasing [A] drives reaction to the right.
In other words, it alters G. (more negative)

$\Delta G = 0$ when all conc's are at equilibrium.

We measure G, for practical reasons, RELATIVE TO a reference state (as we did for $\bar{H}_f^\circ$)

Chemist's standard state → everything at a conc (activity) = 1.

In water, this is an inconvenient standard (for example $[H^+] = 1$ yields pH = 0 (not physiological)).

Chemists usually use 25°C as ref temp.

Biochemist's standard state uses pH = 7.0

We will soon be leaving (mostly) the simple world of ideal gases.

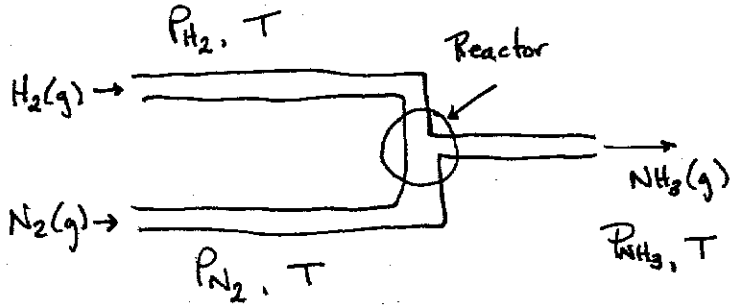
Molecules (solutes, solvents) interact. We saw this for protein folding.

Things like solvation destroy our uniform view of the solvent.

Before we leave ideal gases, let's look at a few more things:

Haber process – industrial production of $NH_3(g)$
(soil organisms also fix N to $NH_3(g)$)

Isothermal



Initial State
P_{N_2}, P_{H_2}, T
x moles $H_2(g)$
y moles $N_2(g)$

→

Final State
P_{NH_3}, T
z moles $NH_3(g)$

4 things to know

Remember that for pressures other than 1 atm, we have to adjust params, as with:

$$N_2(g)\ H_2(g)\ P_{N_2}\ P_{H_2} \xrightarrow{\Delta G_T} NH_3(g)\ P_{NH_3}$$

$\Delta G_1 \downarrow$ $\uparrow \Delta G_2$

$$N_2(g)\ H_2(g)\ [1\ atm] \xrightarrow[\Delta G^\circ_T]{} NH_3(g)\ [1\ atm]$$

$$\Delta G_T = \Delta G_1 + \Delta G^\circ_T + \Delta G_2$$

Chemical Reaction

$$\tfrac{1}{2} N_2(g, P_{N_2}) + \tfrac{3}{2} H_2(g, P_{H_2}) \xrightarrow{\Delta G_T} NH_3(g, P_{NH_3})$$

$$\downarrow \Delta G_1 \qquad\qquad \uparrow \Delta G_2$$

$$\tfrac{1}{2} N_2(g, 1\,atm) + \tfrac{3}{2} H_2(g, 1\,atm) \xrightarrow[\Delta G_T^\circ]{} NH_3(g, 1\,atm)$$

ΔG_1

$$\Delta G_1 = \tfrac{1}{2}\left[RT \ln \frac{1\,atm}{P_{N_2}}\right] + \tfrac{3}{2}\left[RT \ln \frac{1\,atm}{P_{H_2}}\right]$$

(P_2 = 1 atm, P_1 = P_{H_2})

$$(G_2 - G_1 = nRT \ln P_2/P_1) \leftarrow \text{From last chapter}$$

$$\Delta G_2 = RT \ln \frac{P_{NH_3}}{1\,atm}$$

$$\Delta G_T = \Delta G_1 + \Delta G_T^\circ + \Delta G_2$$

$$= \tfrac{1}{2}\left[RT \ln \frac{1\,atm}{P_{N_2}}\right] + \tfrac{3}{2}\left[RT \ln \frac{1\,atm}{P_{H_2}}\right] + \Delta G_T^\circ + RT \ln \frac{P_{NH_3}}{1\,atm}$$

$$= \Delta G_0^T + RT \ln \frac{P_{NH_3}}{(P_{N_2}^{1/2})(P_{H_2}^{3/2})}$$

This relates ΔG_T at arbitrary pressures to ΔG_0^T and the current partial pressures (concentrations).

Generally

For $aA + bB \rightarrow cC + dD$

We set: $$\Delta G_T = \Delta G_T^\circ + RT \ln \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_b^B} = \Delta G_T^\circ + RT \ln Q$$

So specification of concentrations of ALL players is important to specifying ΔG_T.

Le Chatelier comes from there.

At equilibrium, we know that $\Delta G = 0$

$$\therefore \Delta G_T = 0 = \Delta G_T^\circ + RT \ln \frac{P_{C,eq}^c \, P_{D,eq}^d}{P_{A,eq}^a \, P_{B,eq}^b} = \Delta G_T^\circ + RT \ln K_{eq}$$

where $P_{C,eq}$ $P_{A,eq}$ are the equilibrium pressures.
$P_{D,eq}$ $P_{B,eq}$

So we define $K_{eq} = \dfrac{P_{C,eq}^c \cdot P_{D,eq}^d}{P_{A,eq}^a \cdot P_{B,eq}^b}$

Now we know that:

$$\Delta G_T^\circ = -RT \ln K_{eq}$$

Can substitute back in big equation:

$$\Delta G_T = -RT \ln K_{eq} + RT \ln Q$$

$$= RT \ln \frac{Q}{K}$$

This relates total free energy (potential for spontenaity) for a reaction, to measurable quantities (partial pressures/concentrations) at equilibrium

Also note: $\Delta G^\circ_T = -RT \ln K_{eq}$ ← special case of the more complete equation prior (ie. for $\Delta G = 0$)

leads to $K_{eq} = e^{-\Delta G^\circ / RT}$

Now leave the world of ideal gases.

Why? → Because in liquids and solids, molecules interact (violates primary assumption of "IDEAL")

Solutions and solids are "non-Ideal"

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Tells us about Le Chatelier

when Q is such that $-RT \ln Q = \Delta G^\circ$

then we have equilibrium → no chemical potential

If Q is such that $\Delta G < 0$

then the reaction can be spontaneous to the right (potential!)

If Q is such that $\Delta G > 0$, then spontaneous to left