10/6/99

Teaser →

Ever wonder why:

$$K = \underbrace{e^{-\Delta G/RT}}_{\text{UNITLESS}}$$

OR $\Delta G = -RT \ln K$

what is log of Something with units?

Example

$$K_{eq} = \frac{A^2B}{C}$$ if A, B, and C are all in molar, then K should have units of $(\text{molar})^2$.

What gives?

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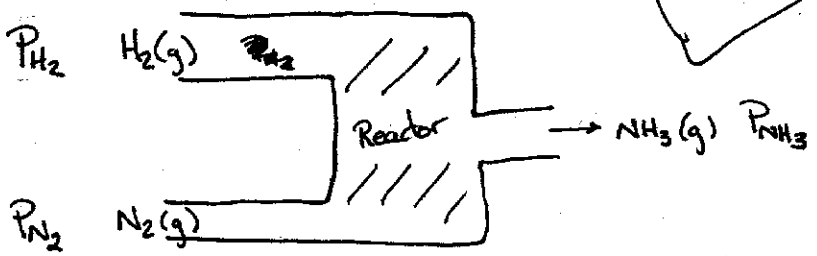
Re-cap → Haber Process

$$\Delta G_T = \Delta G_T^\circ + RT \ln \frac{P_{NH_3}}{P_{N_2}^{1/2} P_{H_2}^{3/2}}$$



Last time we calculated ΔG_T for this process for arbitrary P_{H_2} P_{N_2} and P_{NH_3} at some temperature

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$$

The answer is independent of what happens inside "Reactor." There may be ultra-high temperatures or pressures. They may fluctuate, etc.

The thermodynamics is unchanged → WHY?

(The kinetics, however, may well depend on these!)

In general, at equilibrium:

$$0 = \Delta G_T^\circ + RT \ln K_{eq}$$

etc. Can calculate K_{eq} from ΔG_T°, which we can calculate as before Tables A.6-A.7

Nonideal Behaviour → liquids and solids
(and some real gases!)

$$H_2O\,(\ell) \rightleftharpoons H^+(aq) + OH^-(aq)$$

Using Table A.5

$$\Delta G^\circ_{298} = 79.885\ kJ$$

and then $K_{eq} = e^{-\Delta G^\circ/RT} = 1.011 \times 10^{-14}$

Experiment yields 1.008×10^{-14} (pure water)

Adding KCl changes this:

Experimentally, adding

0.01 M KCl	$K_{eq} = 1.24 \times 10^{-14}$
or 1.0 M KCl	$K_{eq} = 2.8 \times 10^{-14}$

Considering that water has $[H_2O] \approx 55\ M$,
the addition of 0.01 M KCl doesn't exert
its effect by changing conc of water directly.

Rather, adding KCl requires much more than
1 equivalent of water to order around
the ions. This lowers conc of free water

Unlike ideal gases, here the two components
INTERACT!

The actual conc of water is still effectively 55 M, but the <u>effective</u> concentration (which is what really matters) changes.
Same is true for $[H^+]$ and $[OH^-]$.

The effective conc is "activity" and that's what we ought to use in calc's.

But that's too hard, so we assume that

$$[A] \approx a_A$$

$[A]$: we can determine; units, but relative

a_A: what's really these; unitless

[These non-ideal interactions are essential to life (proteins, cells, etc.) as we know it!
→ most proteins are not "happy" in pure water!]

Activities — the real thing $aA + bB \rightarrow cC + dD$

So now $Q = \dfrac{a_C^c \, a_D^d}{a_A^a \, a_B^b}$

and $K_{eq} = \dfrac{(a_C^{eq})^c (a_D^{eq})^d}{(a_A^{eq})^a (a_B^{eq})^b}$

For each component, we can write: $\bar{G}_A = \bar{G}_A^\circ + RT \ln a_A$

- $\bar{G}_A$: free energy per mole A
- $\bar{G}_A^\circ$: standard free energy per mole A
- a_A: activity of A

Define:

$\mu_A = \bar{G}_A$ ← partial molal free energy (LATER)

↑ Chemical potential

So just as ΔH_f° ($\bar{H}^\circ$) is relative to a standard state, so too is $\bar{G}_A$ or μ_A

This is why μ_A is unitless.

This also explains why we can have

$K = e^{-\Delta G^\circ / RT}$ which should be unitless

But can have

$K = \dfrac{A^2 B}{C}$ which does not appear to be unitless.

So back to reality.

we will worry about units for K
except when we deal with $\Delta G = -RT \ln K$.

Relate activity to things that we measure,

Gases Pressure $a_A = \gamma_A P_A = \left(\frac{P_A}{P_A^{\text{standard state}}} \right)$

γ_A: activity coefficient; P_A: partial pressure

γ is sort of like $\frac{1}{\text{standard state}}$

Standard state is 1atm, but with no intermolecular interactions (ie limit as $P_A \to 0$)

$$\gamma_A \to 1 \quad \text{as} \quad P_A \to 0$$

Solids (and PURE liquids)

Standard state is the pure substance at 1 atm pressure.

So since the species is the same as the standard state, the ratio is 1

$$a_A = 1$$

This is why we can leave solids out of equilibrium constants (remember solubility products?)

Solutions

As we saw before, the effective concentration of species A in solution might be a function of conc's of other species.

Concentration

We'll still say → $a_A = \gamma_A C_A$

this means that γ_A depends on the Complete make-up of the solution!

Mole Fraction

Typically used for liquids mixed with liquids

Pure liquid A is defined as the standard state

$$\chi_A = \frac{\#\text{moles A}}{\sum \#\text{moles } z_i} = \frac{n_A}{n_T}$$

$$a_A = \gamma_A \chi_A \qquad \lim_{\chi_A \to 1} a_A = \chi_A$$

or

as $\chi_A \to 1$ (pure)

$\gamma_A \to 1$ (ideal)

SUMMARIZE

≈ IDEAL

Very dilute solution: $a_{solvent} = 1$

Therefore we leave water out of K's and Q's.

Dilute solution: $a_{solvent} = X_{solvent}$

(Very dilute is a special case of "dilute." If water is 55M and we have 0.01 M ethanol in it, then $X_{water} = \frac{55M}{55.01\ M} = 1.000$ ↖ not exactly, but you get the picture.)

In contrast, wine might be better treated as a dilute solution.

Real solution: $a_{solvent} = \gamma X_{SOLVENT}$

in this case, γ now includes intermolecular interactions (NON-ideal).

MOLARITY SCALE: $\frac{\text{moles solute}}{\text{total volume (L)}}$

$$a_A = \gamma_A C_A$$

the solute standard state is the state that has the properties (ideal) of a very dilute solution, but then extrapolated to 1.0 M.

Biochemist's Standard State

(typically let $a_{water} \approx 1$)

Problem: water can dissociate to yield H^+ (ie water comes at different pH's)

Solution: Choose pH=7 as the standard state (reference), so that $a_{H^+} = 1$

Denote parameters using this reference as $\Delta G'$ and $\Delta G^{\circ\prime}$

You can calculate at other pH's, it's just that the reference state is pH=7

$$HOAc\ (aq) \rightleftharpoons H^+\ (aq) + OAc^-\ (aq)$$

$$K = \frac{(a_{H^+})(a_{OAc^-})}{a_{HOAc}} = \frac{(\gamma_+ C_{H^+})(\gamma_- C_{OAc^-})}{\gamma_{HOAc} C_{HOAc}}$$

$$= \frac{\gamma_+ \gamma_-}{\gamma_{HOAc}} \frac{C_{H^+} C_{OAc^-}}{C_{HOAc}} = \frac{\gamma_+ \gamma_-}{\gamma_{HOAc}} K_c$$

and

$$K_c = \frac{(C_{H^+})(C_{OAc^-})}{C_{HOAc}}$$