

The Deal with Equilibrium : Everything Needed for Problem Set 7

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EQUILIBRIUM EXPRESSIONS

For any reaction $aA_{(g)} + bB_{(g)} \longrightarrow cC_{(g)} + dD_{(g)}$,

$$K_{equilibrium} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

K_p takes pressures, K_c takes concentrations (generally M = mol/L). These are both equilibrium constants.

Only *aqueous* and *gaseous* substances appear in equilibrium expressions, since solids and liquids have constant concentrations, and equilibrium expressions deal only with variable concentrations. If you have a product or reactant that is solid or liquid, just leave it out. We usually assume in equilibrium problems that solids and liquids are present in excess.

The only thing on which K depends is *temperature*.

INTERPRETING THE VALUE OF K

If K is large (greater than 100), mostly products will be present at equilibrium (“product-favored reaction”).

If K is small (less than 0.01), mostly reactants will be present at equilibrium (“reactant-favored reaction”).

If K is medium (between 0.01 and 100), there will be significant amounts (concentration or pressure) of both products and reactants at equilibrium.

MANIPULATION OF K

When a reaction is reversed, K is inverted (take the reciprocal, $\frac{1}{K}$ or K^{-1}).

When a reaction is multiplied by a constant, K is raised to that power.

When reactions are added, K 's are multiplied.

THE REACTION QUOTIENT : Q

For any reaction $aA_{(g)} + bB_{(g)} \longrightarrow cC_{(g)} + dD_{(g)}$, *whether at equilibrium or not*,

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

If $Q > K$, then reaction is proceeding to the left (backwards, towards reactants)

If $Q < K$, then reaction is proceeding to the right (to products)

If $Q = K$, then the reaction is at equilibrium!

LE CHATELIER'S PRINCIPLE

Principle: When a system is *stressed*, it will shift in the direction that reduces the stress, moving to a new equilibrium state.

Potential Stresses

- Pressure/volume changes
- Addition/removal of aqueous or gaseous reactant or product
- Temperature changes

Fake Stresses

- Addition/removal of a catalyst
- Addition/removal of a solid or liquid reactant or product
- Addition/removal of other non-reacting substances

VAN 'T HOFF EQUATION

This can be used to estimate the value of K at different temperatures. (However, it has some inherent inaccuracy in its assumption that ΔH_{rxn}^0 is the same at all temperatures, which is sometimes not quite true.)

$$\ln\left(\frac{K_2}{K_1}\right) = \left(\frac{\Delta H_{rxn}^0}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Generally, you'd want to convert ΔH_{rxn}^0 to Joules and use $R = 8.314 \text{ J/mol}\cdot\text{K}$.