Le Chatelier’s principle

When a system at equilibrium is subjected to a disturbance, its composition adjusts so as to tend to minimize the effect of the disturbance

⇒ When a system at equilibrium is heated,

a) the equilibrium composition of an exothermic reaction will shift towards reactants,

b) while the equilibrium composition of an endothermic reaction will shift towards products

Why?

$$\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$$

⇒ qualitatively:

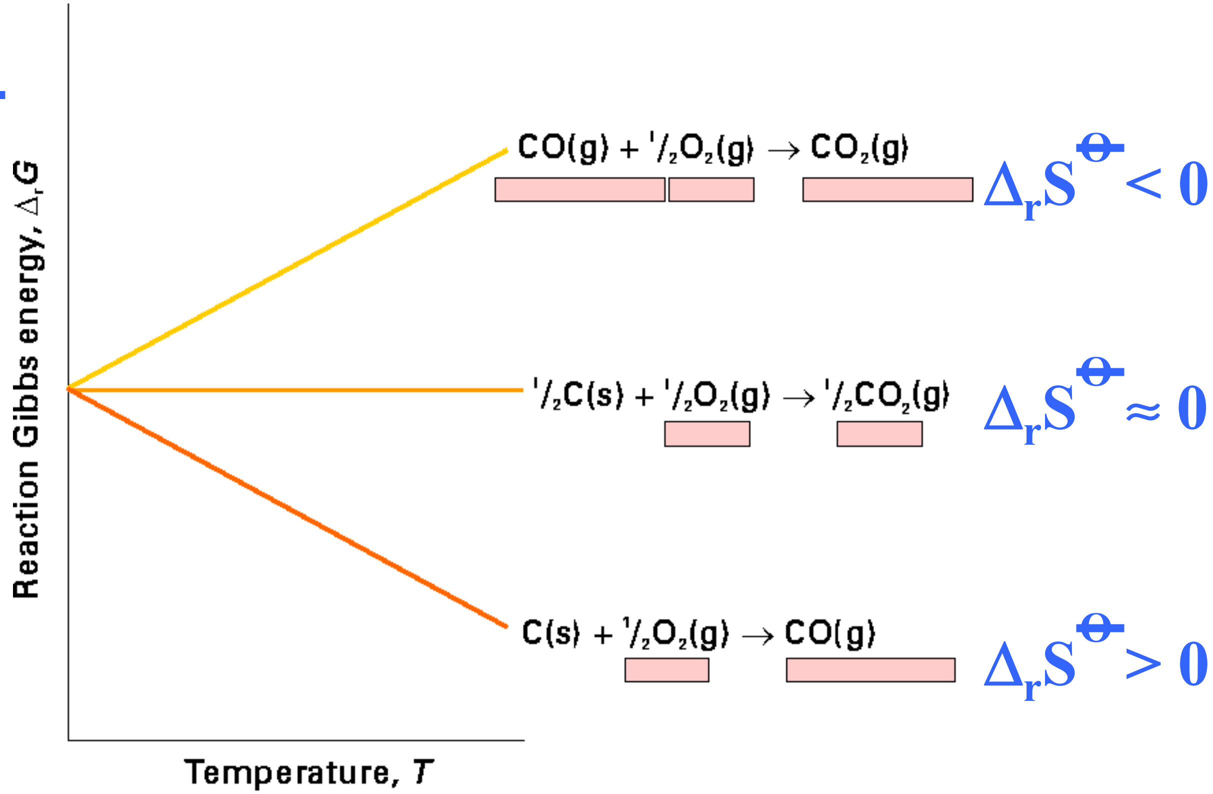
change in $\Delta_r G^{\ominus}$ = -(change in T) x $\Delta_r S^{\ominus}$

and neither reaction enthalpy nor entropy shall vary with T

Temperature dependence

change in $\Delta_r G^\ominus$
$= -$(change in T) x $\Delta_r S^\ominus$

If T↑ (T' > T):
- exothermic reaction shifts towards reactants (K' < K)
- endothermic reaction shifts towards products (K' > K)



Effect on K:

$$\ln K = -\frac{\Delta_r G^\ominus}{RT} = -\frac{\Delta_r H^\ominus}{RT} + \frac{\Delta_r S^\ominus}{R}$$

$$\ln K' = -\frac{\Delta_r H^\ominus}{RT'} + \frac{\Delta_r S^\ominus}{R}$$

$$\Rightarrow \boxed{\ln K' - \ln K = \ln\frac{K'}{K} = \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)}$$

van't Hoff equation

The effect of compression

Le Chatelier:

When a system at equilibrium is compressed,
the composition of a gas-phase equilibrium adjusts
so as to reduce the number of molecules in the gas phase

$$\boxed{\Delta_r G^{\ominus} = -RT \ln K}$$

BUT: $\Delta_r G^{\ominus}$ is measured at 1 bar and
DOES NOT CHANGE WITH PRESSURE
⇒ K IS INDEPENDENT OF PRESSURE

Example: $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$

$$K = \frac{p_{NH_3}{}^2}{p_{N_2} p_{H_2}{}^3} \xrightarrow{\text{pressure doubled}} K' = \frac{(2p_{NH_3})^2}{(2p_{N_2})(2p_{H_2})^3} = \frac{1}{4}K$$

BUT: K and K' must be identical ⇒ partial pressures must adjust ⇒ more NH_3 formed (Haber-Bosch process)

Consequences of equilibrium

Atkins, Chapter 8

reaction aA + bB → cC + dD $\Rightarrow$ $K = \dfrac{a_C^{\;c} \times a_D^{\;d}}{a_A^{\;a} \times a_B^{\;b}}$

K is truly a constant (@ constant T): retains its value even if individual activities change ⇒ adjustment

E.g., proton transfer equilibria following Brønsted-Lowry theory:

$\mathrm{HA(aq)} + \mathrm{H_2O(aq)} \rightleftharpoons \mathrm{A^-(aq)} + \mathrm{H_3O^+(aq)} \Rightarrow K = \dfrac{a_{A^-} \times a_{H_3O^+}}{a_{HA} \times a_{H_2O}}$

acid

conjugate base

$\mathrm{B(aq)} + \mathrm{H_2O(aq)} \rightleftharpoons \mathrm{BH^+(aq)} + \mathrm{OH^-(aq)} \Rightarrow K = \dfrac{a_{BH^+} \times a_{OH^-}}{a_B \times a_{H_2O}}$

base

conjugate acid

Proton transfer equilibria are fast, highly reversible, and important in biology

Brønsted-Lowry theory

Definition: $$\boxed{pH = -\log a_{H_3O^+}}$$

acidicity constant:

$$K = \frac{a_{A^-} \times a_{H_3O^+}}{a_{HA} \times a_{H_2O}} \xrightarrow[\mathbf{a_{H2O} = constant}]{} K_a = \frac{a_{A^-} \times a_{H_3O^+}}{a_{HA}}$$

$$pK_a = -\log K_a$$

basicity constant:

$$K = \frac{a_{BH^+} \times a_{OH^-}}{a_B \times a_{H_2O}} \xrightarrow[\mathbf{a_{H2O} = constant}]{} K_b = \frac{a_{BH^+} \times a_{OH^-}}{a_B}$$

$$pK_b = -\log K_b$$

Autoprotolysis equilibrium of water:

autoprotolysis constant:

$$2\,H_2O(aq) \rightleftharpoons OH^-(aq) + H_3O^+(aq) \Rightarrow K_w = a_{H_3O^+} \times a_{OH^-}$$

$$pK_w = -\log K_w$$

a ≈ [ ]

$$K_w = 10^{-14}\ (@\,25^\circ C) \Rightarrow pK_w = 14 = pH + pOH$$

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