VC210

Chemical Equilibrium

Zhao Yiqing

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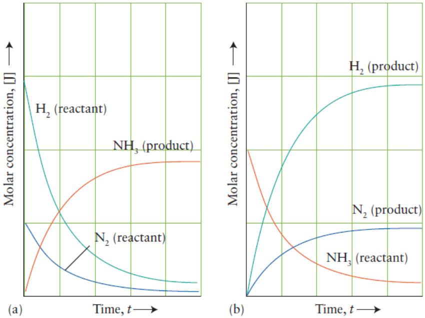
The Reversibility of Reactions

1. All chemical equilibria are dynamic equilibria.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

2. Chemical reactions reach a state of dynamic equilibrium in which the rates of forward and reverse reactions are equal and there is no net change in composition.



Equilibrium and the Law of Mass Action

1. The Law of Mass Action:
   For the reaction
   $$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$
   between the ideal gases, we can get the equilibrium constant K
   $$K = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$
   which is characteristic of the reaction at a given temperature, with P_J denoting the numerical values of the partial pressures in bar at equilibrium.
2. For reactions consists of substances other than gases, such as
   $$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
   we consider the equilibrium constant K as
   $$K = P_{CO_2}$$

Equilibrium and the Law of Mass Action

3. To get a more general idea about the equilibrium constant, we introduce a new concept of activity a_P of a substance J:

Substance	Activity	Simplified form
ideal gas	$a_J = P_J/P^\circ$	$a_J = P_J$
solute in a dilute solution	$a_J = [J]/c^\circ$	$a_J = [J]$
pure solid or liquid	$a_J = 1$	$a_J = 1$

4. All activities are pure numbers and unitless.
5. To calculate the equilibrium constant for equations with phase not specified, such as

$$\mathrm{aA + bB \rightleftharpoons cC + dD}$$

we can get the equilibrium constant K as

$$K = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}$$

6. Equilibrium constant of a certain reaction can be changed only by varing the temperature.

The Origin of Equilibrium Constants

1. Define the reaction quotient Q as

$$Q = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}$$

2. For differences between K and Q, the activities used in K must be measured at equilibrium.
3. Relative thermodynamics reactions:

$$\Delta G_r = \Delta G_r^\circ + RT \ln Q = -RT \ln K + RT \ln Q$$

$$\Delta G_r^\circ = -RT \ln K(at\ equilibrium)$$

$$K = e^{-\frac{\Delta G_r^\circ}{RT}}$$

   i. If ΔG_r° is negative, then $\ln K$ must be positive and therefore $K > 1$; products are favored at equilibrium.
   ii. If ΔG_r° is positive, then $\ln K$ must be negative and therefore $K < 1$; reactants are favored at equilibrium.

The Origin of Equilibrium Constants

4. For relationships between Q and K:
   1. If $Q < K$, ΔG_r is negative; the reaction has a tendency to proceed toward products.
   2. If $Q = K$, ΔG_r is zero; the reaction has its equilibrium.
   3. If $Q > K$, ΔG_r is positive; the reverse reaction is spontaneous.

Multiples of the Chemical Equation

Chemical Equation	Equilibrium Constant
$\mathrm{aA + bB \rightleftharpoons cC + dD}$	K_1
$\mathrm{cC + dD \rightleftharpoons aA + bB}$	$K_2 = \frac{1}{K_1} = K_1^{-1}$
$\mathrm{N(aA + bB \rightleftharpoons cC + dD)}$	$K_3 = K_1^N$

Table: Relations Between Equilibrium Constants

Composite Equations

Chemical Equation	Equilibrium Constant
$\mathrm{aA + bB \rightleftharpoons cC + dD}$	K_1
$\mathrm{eE + fF \rightleftharpoons gG + hH}$	K_2
$\mathrm{aA + bB + eE + fF \rightleftharpoons cC + dD + gG + hH}$	$K_3 = K_1 K_2$

Table: Relations Between Equilibrium Constants

Molar Concentrations of Gases

1. We determine:
   $K_P = equilibrium\ constant\ in\ terms\ of\ pressure$
   $K_c = equilibrium\ constant\ in\ terms\ of\ concentration$
2. The relationship between K_P and K_c is

$$K_P = (RT)^{\Delta n} K_c$$

where

$$\Delta n = \sum n_{products} - \sum n_{reactants}$$

The Extent of Reaction

1. Large values of K (larger than about 10^3): equilibrium favors the products.
2. Intermediate values of K (approximately in the range 10^{-3} to 10^3): neither reactants nor products are strongly favored at equilibrium.
3. Small values of K (smaller than about 10^{-3}): equilibrium favors the reactants.

Calculations with Equilibrium Constants

	Species 1	Species 2	Species 3	...
initial composition				...
change in composition				...
equilibrium composition				...

Calculations with Equilibrium Constants

Question 1. Suppose that there are 3.12 g of PCl_5 in a reaction vessel of volume 500 mL and allow the sample to reach equilibrium with its decomposition products PCl_3 and Cl_2 at $250^\circ C$, when $K = 78.3$ for the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. Find the composition of the equilibrium mixture.

Calculations with Equilibrium Constants

Step 1. Calculate the initial partial pressure of PCl_5.

$$n_{\mathrm{PCl5}} = \frac{3.12g}{208.24g \cdot mol^{-1}} = \frac{3.12}{208.24} mol = 0.0150 mol$$

$$P_{\mathrm{PCl5}} = (0.0150 mol) \times \frac{(8.3145 \times 10^{-2} L \cdot bar \cdot K^{-1} \cdot mol^{-1}) \times 523K}{0.500L}$$
$$= 0.130 bar$$

Calculations with Equilibrium Constants

Step 2. Write the equilibrium expression and set up the equilibrium table.

$$\mathrm{PCl_5(g)} \rightleftharpoons \mathrm{PCl_3(g)} + \mathrm{Cl_2(g)} \qquad K = \frac{P_{\mathrm{PCl_5}} P_{\mathrm{Cl_2}}}{P_{\mathrm{PCl_3}}}$$

	PCl_5	PCl_3	Cl_2
initial pressure	1.30	0	0
change in pressure	$-x$	$+x$	$+x$
equilibrium pressure	$1.30 - x$	$+x$	$+x$

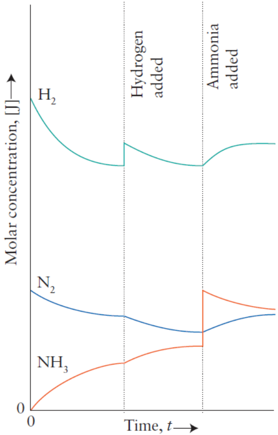
Then we can get the equation

$$K = \frac{x^2}{1.30 - x} = 78.3$$

$$x = 1.28 \text{ or } -79.6 \text{(abandoned)}$$

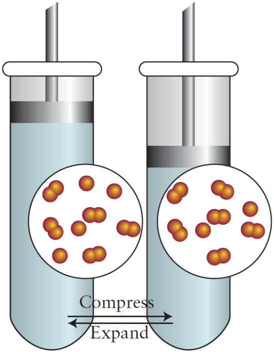
Adding and Removing Reagents

Le Chatelier's Principle: When a stress is applied to a system in dynamic equilibrium, the equilibrium tends to adjust to minimize the effect of the stress.



Compressing a Reaction Mixture

Compression of a reaction mixture at equilibrium tends to drive the reaction in the direction that reduces the number of gas-phase molecules; increasing the pressure by introducing an inert gas has no effect on the equilibrium composition.



Temperature and Equilibrium

$$\Delta G_1^\circ = -RT \ln K_1$$

$$\Delta G_2^\circ = -RT \ln K_2$$

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

1. If the reaction is endothermic, an increase in temperature favors the formation of products.
2. If the reaction is exothermic, an increase in temperature favors the formation of reactants.

Thank you!