

5. Chemical Equilibrium

5.1 Dynamic equilibrium

We often speak of systems at equilibrium. This is a state where the properties of the system – including chemical composition – do not change with time. As such, it seems as though all chemical reactions have ceased at equilibrium. But this is not so - chemical reactions continue. For every forward reaction, there is a reverse reaction. The rate of a forward reaction generally depends on the concentrations of reactants, while the rate of a reverse reaction depends on the concentrations of products (partial pressures for gas reactions). When these rates are unequal, net reaction proceeds, changing the concentrations of reactants and products such that the rates approach each other. Chemical equilibrium occurs when the rate of forward reaction equals the rate of reverse reaction, and there is no further net reaction even though the forward and reverse reactions continue.

All reactions are equilibrium reactions. However, for some reactions, products are strongly favored. In such a case, the rate of forward reaction exceeds the reverse reaction until almost no reactant remains – the reaction essentially goes to completion. When the reactants are strongly favored, no reaction is observed. As seen in Section 5.3, there are cases between these extremes, reactions where neither reactant nor product concentration is negligible at equilibrium. These reactions are characterized by an *equilibrium constant*, which is neither extremely big nor extremely small.

5.2 Equilibrium constant

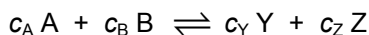
At equilibrium, the concentrations of dissolved species, and partial pressures of gases, stop changing. Sets of experiments show that the final equilibrium concentrations of reactants and products (consider reactions of aqueous species, for example) depend on the initial concentrations – i.e., the concentrations at the start of the experiment. However, there is a combination of concentrations that is the same for every experiment performed at the same temperature. The value of this combination of concentrations is called the equilibrium constant.

Careful studies show that the equilibrium constant is actually a combination of reactant and product *activities*, a . For a species A in solution, at low concentration, the activity is approximately equal to the concentration of the species, $[A]$ in mol L^{-1} . For a gas, the activity is approximately the gas partial pressure, p_A in atm. For pure (or almost pure) liquids and solids, the activity is approximately 1. We take these approximations as exact, and henceforth adopt the following definition the activity, a_A , of species A:

$$a_A = \begin{cases} [A] & \text{for A in solution} \\ p_A & \text{for A in the gas phase} \\ 1 & \text{for pure liquid or solid A} \end{cases} \quad 5.1$$

The units of $[A]$ and p_A are mol L^{-1} and atm, respectively. However, these units are dropped from activity; activity is dimensionless because an activity is a concentration (or a pressure) divided by a standard concentration (or pressure) of 1. The *standard conditions* for chemical reactions (as defined in thermochemical studies – see Chapter 6) are 1 mol L^{-1} concentration of dissolved species and 1 atm partial pressure for gases. Thus, the activity of an aqueous species is really $[A] / (1 \text{ mol L}^{-1})$. It is the concentration relative to its value under standard conditions, 1 mol L^{-1} . Further, the activities of pure liquids and solids are taken to be 1, so these species do not appear in equilibrium constant expressions (see below).

The equilibrium constant, K , for the reaction,



is given by

$$K = \frac{a_Y^{c_Y} a_Z^{c_Z}}{a_A^{c_A} a_B^{c_B}} \quad 5.2$$

where a_A , a_B , a_Y and a_Z are the activities of A, B, Y and Z under equilibrium conditions, and c_A , c_B , c_Y and c_Z are the stoichiometric coefficients of A, B, Y and Z, respectively. Moreover, any combination of a_A , a_B , a_Y and a_Z satisfying this equation constitutes equilibrium conditions. The equilibrium constant depends only temperature.

For more general reactions, there are additional $a_X^{c_X}$ factors in the numerator, if there are additional products; and in the denominator, if there are additional reactants. Examples are provided as follows:

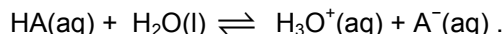
Reaction	Equilibrium constant
$\text{Br}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{BrCl}(\text{g})$	$K = \frac{p_{\text{BrCl}}^2}{p_{\text{Br}_2} p_{\text{Cl}_2}}$
$\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \rightleftharpoons 2 \text{HI}(\text{g})$	$K = \frac{p_{\text{HI}}^2}{p_{\text{H}_2}}$
$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$	$K = \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} p_{\text{H}_2}^3}$
$\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2 \text{OH}^{-}(\text{aq})$	$K = [\text{Ca}^{2+}][\text{OH}^{-}]^2$
$\text{HClO}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{ClO}^{-}(\text{aq}) + \text{H}_3\text{O}^{+}(\text{aq})$	$K = K_a = \frac{[\text{H}_3\text{O}^{+}][\text{ClO}^{-}]}{[\text{HClO}]} \quad \text{or} \quad \frac{[\text{H}^{+}][\text{ClO}^{-}]}{[\text{HClO}]}$
$\text{NaF}(\text{s}) \rightleftharpoons \text{Na}^{+}(\text{aq}) + \text{F}^{-}(\text{aq})$	$K = K_{sp} = [\text{Na}^{+}][\text{F}^{-}]$

The last two examples show named equilibrium constants, K_a and K_{sp} , the acid ionization constant and the solubility product, respectively.

In general, acids are characterized by the acid ionization constant,

$$K_a = \frac{[\text{H}_3\text{O}^{+}][\text{A}^{-}]}{[\text{HA}]}, \quad 5.3$$

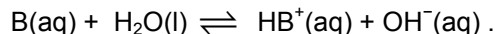
the equilibrium constant for the acid ionization reaction,



Bases are characterized by the base ionization constant,

$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}, \quad 5.4$$

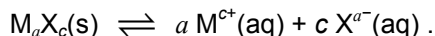
the equilibrium constant for the base ionization reaction,



Salts are characterized by the solubility product,

$$K_{sp} = [\text{M}^{c+}]^a [\text{X}^{a-}]^c \quad 5.5$$

the equilibrium constant for the dissolution of the salt,



Example 5.1: Write down the equilibrium constant, K , for each of the following reactions.

- (a) $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- (b) $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$
- (c) $\text{NO}(\text{g}) + \text{O}_3(\text{g}) \rightleftharpoons \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
- (d) $\text{Cl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{HClO}(\text{aq})$
- (e) $\text{Cl}_2(\text{g}) + 2 \text{Fe}^{2+}(\text{aq}) \rightleftharpoons 2 \text{Cl}^-(\text{aq}) + 2 \text{Fe}^{3+}(\text{aq})$

Approach: Look for gases or aqueous species. The equilibrium constant is constructed from the partial pressures of gases and the concentrations of aqueous species, raised to the associated stoichiometric coefficients in the balanced chemical reaction. Products appear in the numerator, while reactants appear in the denominator.

(a) $K = p_{\text{CO}_2}$

The equilibrium constant is just the partial pressure of carbon dioxide. K here is the vapour pressure of solid carbon dioxide. In an enclosed space, $\text{CO}_2(\text{s})$ will sublime until the partial pressure of $\text{CO}_2(\text{g})$ equals K and the solid and gas are in equilibrium.

(b) $K = p_{\text{NH}_3} p_{\text{H}_2\text{S}}$

$\text{NH}_4\text{HS}(\text{s})$ does not appear in the equilibrium constant because it is a pure solid. All solids and liquids you will encounter in chemical reactions are pure (water, in aqueous reactions, is treated as though it were pure).

(c) $K = \frac{p_{\text{NO}_2} p_{\text{O}_2}}{p_{\text{NO}} p_{\text{O}_3}}$

(d) $K = \frac{[\text{H}^+][\text{Cl}^-][\text{HClO}]}{[\text{Cl}_2]}$

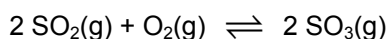
H₂O(l) does not appear. It is treated as a pure liquid. The concentration of pure water, [H₂O], is about 56 mol L⁻¹. Changes in this value caused by dissolved aqueous species are small, and neglected.

$$(e) \quad K = \frac{[\text{Cl}^-]^2 [\text{Fe}^{3+}]^2}{p_{\text{Cl}_2} [\text{Fe}^{2+}]^2}$$

This reaction has a gas and three aqueous species. In this case, the equilibrium constant is constructed from a partial pressure and three concentrations. Note the stoichiometric coefficients in the exponents.

An equilibrium constant is evaluated by preparing an equilibrium mixture of reactants and products, then measuring the resulting concentrations and partial pressures. The value of K obtained does not depend on how the mixture was prepared. It depends only on temperature. Thus, temperature is generally noted when an equilibrium constant is given.

Once an equilibrium constant is known, an unknown concentration or partial pressure can be determined in an equilibrium mixture – if the other concentrations and partial pressures are known. For example, the equilibrium constant for the combustion of sulfur dioxide at 350°C is $K = 5.60 \times 10^4$.



If the partial pressures of O₂ and SO₃ are both 0.500 atm, then the partial pressure of SO₂ is given by substituting all known quantities into the equilibrium constant equation and solving for p_{SO_2} . Specifically,

$$K = \frac{p_{\text{SO}_3}^2}{p_{\text{SO}_2}^2 p_{\text{O}_2}} = \frac{0.500^2}{p_{\text{SO}_2}^2 \cdot 0.500} = 5.60 \times 10^4$$

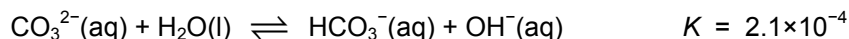
from which we get

$$p_{\text{SO}_2}^2 = \frac{0.500^2}{5.60 \times 10^4 \times 0.500} = 8.92_9 \times 10^{-6}$$

and

$$p_{\text{SO}_2} = 2.99 \times 10^{-3} \text{ atm}$$

Example 5.2: What is the concentration of OH⁻ in an equilibrium solution with [CO₃²⁻] = [HCO₃⁻] = 1.0 mol L⁻¹, given the following equilibrium constant?



Approach: Write down the equilibrium constant expression. Substitute the known concentrations. Solve for the unknown concentration.

$$K = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]} = \frac{1.0 \times [\text{OH}^-]}{1.0} = [\text{OH}^-] = 2.1 \times 10^{-4}$$

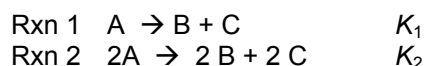
Therefore, [OH⁻] = 2.1 × 10⁻⁴ mol L⁻¹.

Suppose we have a table of equilibrium constants for a set of reactions that does not include a reaction of interest. If the reaction of interest can be expressed as a combination of the tabulated reactions, then the equilibrium constant can be expressed as a product or quotient of the tabulated equilibrium constants.

The simplest case is when the reaction of interest is the reverse of a tabulated reaction. Considering the above definition of the equilibrium constant in terms of activities, one can deduce

$$K_{\text{reverse}} = \frac{1}{K_{\text{forward}}}$$

This follows because the reactants of the reverse reaction are the products of the forward reaction, and vice versa. If the reaction of interest is $2\times$ a tabulated reaction, then the equilibrium constant of interest is the square of the tabulated equilibrium constant. This follows because all the stoichiometric coefficients are doubled if a reaction is doubled. To see this, write down expressions for K_1 and K_2 – the equilibrium constants for the following reactions - and see that $K_2 = K_1^2$.



In general, the equilibrium constant of interest is a product of tabulated equilibrium constants, each raised to a power - the coefficient of the tabulated reaction in the combination required to reproduce the reaction of interest.

$$K = K_1^{n_1} K_2^{n_2} K_3^{n_3} \dots, \quad 5.6$$

where

$$\text{Reaction of interest} = \sum_i n_i (\text{ith tabulated reaction}),$$

n_i is negative for tabulated reactions that need to be reversed.

5.3 The reaction quotient

The above expressions for the equilibrium constant only hold under equilibrium conditions – i.e. the concentrations and partial pressures are for an equilibrium reaction mixture. When a reaction mixture is not at equilibrium, combining the concentrations and partial pressures as they are in the equilibrium constant gives the *reaction quotient*, Q . The reaction quotient can be computed under equilibrium or non-equilibrium conditions. If $Q = K$, then the system is at equilibrium. Otherwise, $Q \neq K$ and there is net forward or reverse reaction.

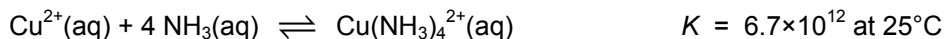
If $Q < K$, there is net forward reaction. Net forward reaction depletes reactants, reducing the denominator of Q . At the same time, product concentrations/partial pressures increase, increasing the numerator of Q . The net effect is an increase in Q . Net forward reaction continues until $Q = K$.

If $Q > K$, there is net reverse reaction. Net reverse reaction increases reactant concentrations/partial pressures, increasing the denominator of Q . At the same time, product is depleted, decreasing the numerator of Q . The net effect is a decrease in Q . Net reverse reaction continues until $Q = K$.

Example 5.3: Consider each of the following reaction mixtures. Is the mixture at equilibrium, or is there net forward or reverse reaction?

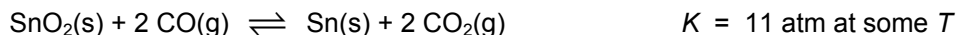
(a) Solid calcium carbonate and calcium oxide at 700°C are in a vessel with 0.1 atm partial pressure carbon dioxide. At 700°C, $K = 0.056$ for the decomposition of $\text{CaCO}_3(\text{s})$ into $\text{CaO}(\text{s})$ and $\text{CO}_2(\text{g})$.

(b) Consider the following equilibrium:



Suppose $[\text{Cu}^{2+}] = [\text{Cu}(\text{NH}_3)_4^{2+}] = 1.0 \text{ mol L}^{-1}$, while $[\text{NH}_3] = 5.0 \times 10^{-4} \text{ mol L}^{-1}$ at 25°C.

(c) Consider the following equilibrium:



Suppose the partial pressure of CO_2 is 3 atm, while that of CO is 1 atm at the required T .

Approach: Compute Q and compare it with K .

(a) $Q = p_{\text{CO}_2} = 0.1 > 0.056$. Therefore, there is net reverse reaction. At this partial pressure, CO_2 in the gas phase combines with available $\text{CaO}(\text{s})$ to form $\text{CaCO}_3(\text{s})$.

(b) Here,

$$Q = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{1.0}{1.0(5.0 \times 10^{-4})^4} = 1.6 \times 10^{13} > K$$

Again, $Q > K$ and there is net reverse reaction.

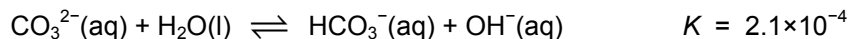
(c) Here,

$$Q = \frac{p_{\text{CO}_2}^2}{p_{\text{CO}}^2} = \frac{3^2}{1} = 9 < 11$$

In this case, $Q < K$ and there is net forward reaction.

5.4 Shift in equilibrium – le Châtelier's principle

Non-equilibrium conditions can result, starting with an equilibrium mixture, by adding or removing a reactant or a product. For example, if we have an equilibrium solution with the reaction



and we dissolve a small amount of $\text{NaOH}(\text{s})$ into the solution, a non-equilibrium initial state results. Increasing the concentration of hydroxide makes Q larger (a factor in the numerator is increased). Since Q is now larger than K , there is net reverse reaction – product concentrations decrease, while the reactant concentration increases. Net reaction continues until $Q = K$ is restored. When equilibrium is re-established, the hydroxide concentration is smaller than it was immediately after the added $\text{NaOH}(\text{s})$ dissolves, but larger than it was before the $\text{NaOH}(\text{s})$ was added.

We can also add a small amount of concentrated sulfuric acid (so as not to significantly change the total volume) to the solution. The added strong acid reacts completely with OH^- present, and reduces the hydroxide concentration. As such, it removes a product from the chemical reaction. This has the effect of making Q smaller. Net forward reaction results until equilibrium is re-established.

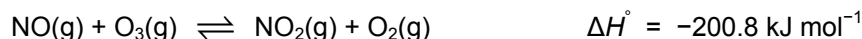
Whether we add or remove product, the net reaction acts to reduce the change imposed on the system – the addition or removal of some hydroxide. The hydroxide concentration moves back towards (but does not reach⁷) its value before the change was imposed. This is a general principle called *le Châtelier's principle*:

When a change is imposed on an equilibrium system, the change is followed by net reaction that reduces the change.

If a reactant is added – in the above example, some $\text{Na}_2\text{CO}_3(\text{s})$ can be dissolved in the solution – le Châtelier's principle tells us that there will be net forward reaction consuming some of the added CO_3^{2-} . This is consistent with reaction quotient considerations. Note that the principle only applies to changes in activity. Changes in the amount of a pure solid or liquid do not affect an equilibrium. Thus, changing the amount of $\text{CaCO}_3(\text{s})$ or $\text{CaO}(\text{s})$ in an equilibrium mixture with $\text{CO}_2(\text{g})$ does not affect the partial pressure of the gas.

Le Châtelier's principle also applies to the effect of changing temperature. The equilibrium constant generally depends upon temperature. Thermodynamics shows that K increases or decreases with temperature in accord with the sign of ΔH (change in enthalpy – see more in Chapter 6). Specifically, K increases with T for endothermic reactions ($\Delta H > 0$), and decreases with T for exothermic reactions ($\Delta H < 0$). If K increases with T , as it does for endothermic reactions, products will be favored at higher T . Thus, increasing T for an endothermic reaction causes net forward reaction until the new (product favored) equilibrium is established. This is consistent with le Châtelier's principle in the following sense: Increasing T makes more heat "available". A net forward endothermic reaction consumes some of this additional heat. In general, the endothermic direction of reaction (the reverse reaction, in the case of an exothermic reaction) is favored with increasing temperature. Thus, reactants are favored at high T in the case of an exothermic reaction.

Example 5.4: Predict the direction each of the following equilibria shifts when the indicated changes are imposed.



- (a) The O_3 partial pressure is increased
- (b) Some NO_2 is removed from the reaction mixture
- (c) The reaction mixture is transferred to a vessel with twice the volume
- (d) Temperature is increased



- (e) The HCl partial pressure is increased
- (f) Some solid NH_4Cl is added to the mixture
- (g) Temperature is decreased

Approach: Is a reactant or product activity changed – i.e., a partial pressure or concentration? If so, apply le Châtelier's principle. If temperature changes, note the sign of the enthalpy of reaction.

- (a) O_3 is a reactant. Increasing its partial pressure results in net forward reaction – to consume some of the added O_3 .

⁷ In the case of an equilibrium with just one activity – for example, the decomposition of $\text{CaCO}_3(\text{s})$ – if the activity is changed, it will return to original value. Otherwise, shifts in other activities will prevent a changed activity from returning to its original value.

- (b) NO_2 is a product. Removing it from the reaction mixture results in net forward reaction. This is a common means of improving product yield. Removing the product from a reaction mixture drives the reaction in the forward direction.
- (c) Doubling the volume of the vessel reduces all partial pressures to 1/2 their initial values. However, this does not change the reaction quotient because there are two partial pressure factors in both the numerator and denominator of Q and they have the same exponents. Decreasing all partial pressures by the same factor thus has no effect on the reaction quotient. Therefore, the system is still at equilibrium. This is consistent with Le Châtelier's principle, which says that the reaction will shift to the side with more moles of gas so as to counter the reduction in total pressure caused by the increase in volume. However, neither forward nor reverse reaction increases the moles of gas. Therefore, the mixture remains at equilibrium.
- (d) The reaction is exothermic. Increasing temperature favors reactants (the endothermic direction of reaction) – i.e., there is net reverse reaction.
- (e) HCl is a product. Increasing its partial pressure results in net reverse reaction.
- (f) $\text{NH}_4\text{Cl(s)}$ is a pure solid. Adding it or removing some of it from the reaction mixture has no effect on the equilibrium as long as some of the solid remains. No net reaction results.
- (g) The reaction is endothermic. Decreasing temperature favors reactant (the exothermic direction of reaction) – i.e., there is net reverse reaction.

The equilibrium constant allows quantitative determination of final equilibrium conditions. Such determinations are carried out by constructing an *ICE* table to relate equilibrium activities to the extent of reaction. This begins with the balanced chemical reaction. Below that are three rows. The first row shows the *initial* (I), non-equilibrium concentrations/partial pressures of reactants and products. The second row expresses the *changes* (C) in these concentrations (that occur upon achieving equilibrium) in terms of the unknown extent of reaction. This row accounts for the stoichiometric coefficients in the reaction. The third row is the sum of the first two rows. It gives the concentrations/partial pressures at *equilibrium* (E). For example, consider the reaction of water vapor and carbon monoxide, both initially at 1.00 atm partial pressure. $K = 0.63$ for this reaction at a certain T .

	$\text{H}_2\text{O(g)}$	+	CO(g)	\rightleftharpoons	$\text{H}_2\text{(g)}$	+	$\text{CO}_2\text{(g)}$
Initial	1.00		1.00		0		0
Change	$-x$		$-x$		$+x$		$+x$
Equilibrium	$1.00 - x$		$1.00 - x$		x		x

Here, x is the *extent of reaction*, appearing as a change in partial pressure. If one of the species had a stoichiometric coefficient greater than 1, it would multiply x in the associated cell. Having expressed the equilibrium concentrations in terms of the unknown x , we construct the equilibrium constant equation in terms of x .

$$K = \left(\frac{p_{\text{H}_2} p_{\text{CO}_2}}{p_{\text{H}_2\text{O}} p_{\text{CO}}} \right)_{\text{eqm}} = \frac{x x}{(1.00 - x)(1.00 - x)} = 0.63$$

from which we get

$$\left(\frac{x}{(1.00 - x)} \right)^2 = 0.63$$

$$\frac{x}{(1.00 - x)} = \sqrt{0.63} = 0.79_4$$

$$x = 0.79_4(1.00 - x)$$

$$x = \frac{0.79_4}{1.79_4} = 0.44_3$$

With $x = 0.44_3$, we can get the equilibrium partial pressures – the bottom row in the ICE table. Specifically,

$$p_{\text{H}_2\text{O}} = p_{\text{CO}} = 1.00 - x = 0.56 \text{ atm}$$

and

$$p_{\text{H}_2} = p_{\text{CO}_2} = x = 0.44 \text{ atm}$$

The above equation for x is easily solved because the right side of the first line is a perfect square (resulting from the reaction stoichiometry and because we started with equal partial pressures of H_2O and CO). For a simple equilibrium, a linear equation might result directly. However, in general, a polynomial equation is obtained. For many important reactions this is a quadratic reaction that can be solved approximately, or exactly using the formula for the solution of a quadratic equation – see below.

Example 5.5: Consider the gas phase equilibrium of hydrogen and iodine,



(a) Suppose a vessel is filled to 0.100 atm of both H_2 and I_2 . What is the partial pressure of HI when equilibrium is established at T ?

(b) Suppose the vessel is filled to 1.00 atm of H_2 and 0.100 atm of I_2 . What is the partial pressure of HI when equilibrium is established at T ?

Approach: Construct an ICE table. Substitute into the equilibrium constant equation and solve for the unknown extent of reaction. Evaluate the equilibrium partial pressures in the third row of the ICE table.

(a)

	H_2	+	I_2	\rightleftharpoons	2HI
Initial	0.100		0.100		0
Change	$-x$		$-x$		$+2x$
Equilibrium	$0.100 - x$		$0.100 - x$		$2x$

Substitute the equilibrium partial pressures into the equilibrium constant equation.

$$K = \frac{p_{\text{HI}}^2}{p_{\text{H}_2} p_{\text{I}_2}} = \frac{(2x)^2}{(0.100-x)(0.100-x)} = 33$$

This equation simplifies.

$$\left(\frac{2x}{(0.100-x)} \right)^2 = 33$$

$$\frac{2x}{(0.100-x)} = \sqrt{33} = 5.7_4$$

$$2x = 5.7_4(0.100-x)$$

$$x = \frac{0.57_4}{7.7_4} = 0.074_2$$

Thus, the final equilibrium partial pressure of HI is

$$p_{\text{HI}} = 2x = 2 \times 0.074_2 = 0.148 \text{ atm}$$

(b)

	H₂	+	I₂	⇌	2 HI
Initial	1.00		0.100		0
Change	- x		- x		+2 x
Equilibrium	1.00 - x		0.100 - x		2 x

Substitute the equilibrium partial pressures into the equilibrium constant equation.

$$K = \frac{p_{\text{HI}}^2}{p_{\text{H}_2} p_{\text{I}_2}} = \frac{(2x)^2}{(1.00-x)(0.100-x)} = 33$$

This equation requires solution of a quadratic equation.

$$\frac{4x^2}{(0.100-1.10x+x^2)} = 33$$

$$4x^2 = 33(0.100-1.10x+x^2)$$

$$29x^2 - 36.3x + 3.3 = 0$$

$$ax^2 + bx + c = 0$$

The solution of this quadratic equation is

$$\begin{aligned}
 x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\
 &= \frac{36.3 \pm \sqrt{36.3^2 - 4 \times 29 \times 3.3}}{2 \times 29} \\
 &= \begin{cases} 1.1_5 \\ 0.098_7 \end{cases}
 \end{aligned}$$

We get two solutions for x . However, only one of them is admissible. The choice of $x = 1.1_5$ yields negative equilibrium partial pressures for H_2 and I_2 . It is an inadmissible solution. Thus,

$$x = 0.098_7$$

is the correct solution, and

$$p_{HI} = 2x = 2 \times 0.098_7 = 0.197 \text{ atm}$$

5.5 Solubility

When the equilibrium corresponds to the dissolution of an ionic solid (a salt), the equilibrium constant is called a solubility product, K_{sp} . The K_{sp} value determines the concentration of the ions in equilibrium with the solid. If excess salt is added to pure water, the resulting cation and anion concentrations are related by the stoichiometric coefficients in the dissolution process.

For example, the equilibrium constant of the reaction,



is K_{sp} for $Ba_3(PO_4)_2(s)$. The overall concentration of the salt is called the *molar solubility*. Thus, the molar solubility of $Ba_3(PO_4)_2(s)$ is 1/3 the barium concentration, or 1/2 the phosphate concentration at equilibrium, as per the stoichiometry of the K_{sp} expression.

Example 5.6: Determine the molar solubilities of the following salts at 25°C. (K_{sp} values are for 25°C.)

- (a) $BaCO_3$ $K_{sp} = 2.6 \times 10^{-9}$
 (b) CaF_2 $K_{sp} = 3.45 \times 10^{-11}$

Approach: Construct an ICE table for the addition of excess solid salt to pure water. Solve for the extent of reaction and evaluate the equilibrium concentrations.

(a)

	BaCO₃(s)	\rightleftharpoons	Ba²⁺(aq)	+	CO₃²⁻(aq)
Initial			0		0
Change			+x		+x
Equilibrium			x		x

Substitute the equilibrium ion concentrations into the solubility product equation.

$$K_{sp} = [\text{Ba}^{2+}][\text{CO}_3^{2-}] = x^2 = 2.6 \times 10^{-9}$$

which gives

$$x = \sqrt{2.6 \times 10^{-9}} = 5.1 \times 10^{-5}$$

At equilibrium,

$$[\text{Ba}^{2+}] = [\text{CO}_3^{2-}] = 5.1 \times 10^{-5} \text{ mol L}^{-1}$$

In this case, the molar solubility is just the barium or carbonate concentration, i.e., $5.1 \times 10^{-5} \text{ mol L}^{-1}$.

(b)

	CaF₂(s)	\rightleftharpoons	Ca²⁺(aq)	+	2 F⁻(aq)
Initial			0		0
Change			+x		+2 x
Equilibrium			x		2 x

Substitute the equilibrium ion concentrations into the solubility product equation.

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2 = x(2x)^2 = 3.45 \times 10^{-11}$$

which gives

$$x = \left(\frac{3.45 \times 10^{-11}}{4} \right)^{1/3} = 2.05 \times 10^{-4}$$

At equilibrium,

$$\begin{aligned} [\text{Ca}^{2+}] &= x = 2.05 \times 10^{-4} \text{ mol L}^{-1} \\ [\text{F}^-] &= 2x = 4.10 \times 10^{-4} \text{ mol L}^{-1} \end{aligned}$$

In this case, the molar solubility is just the calcium concentration or 1/2 the fluoride concentration, i.e. $2.05 \times 10^{-4} \text{ mol L}^{-1}$.

If we attempt to dissolve a salt in a solution that already contains a solvated ion in common with an ion in the salt, less of the salt will dissolve. This is called the *common ion effect*. For example,

consider dissolving $\text{CaCO}_3(\text{s})$ in a saturated solution of $\text{CaF}_2(\text{s})$. $K_{sp} = 3.36 \times 10^{-9}$ for calcium carbonate at 25°C . Construct the ICE table for this process.

	$\text{CaCO}_3(\text{s})$	\rightleftharpoons	$\text{Ca}^{2+}(\text{aq})$	+	$\text{CO}_3^{2-}(\text{aq})$
Initial			2.05×10^{-4}		0
Change			$+x$		$+x$
Equilibrium			$2.05 \times 10^{-4} + x$		x

Note that the initial concentration of calcium is not zero – it is the calcium concentration of a solution saturated in calcium fluoride.

Substitute the equilibrium ion concentrations into the solubility product equation.

$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = (2.05 \times 10^{-4} + x)x = 3.36 \times 10^{-9}$$

which gives

$$x^2 + 2.05 \times 10^{-4}x - 3.36 \times 10^{-9} = 0$$

Using the quadratic formula,

$$\begin{aligned} x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ &= \frac{-2.05 \times 10^{-4} \pm \sqrt{(2.05 \times 10^{-4})^2 + 4 \times 3.36 \times 10^{-9}}}{2} \\ &= \begin{cases} 1.52_6 \times 10^{-5} \\ -2.20_3 \times 10^{-4} \end{cases} \end{aligned}$$

The negative solution produces a negative carbonate concentration at equilibrium and is therefore inadmissible.

At equilibrium,

$$\begin{aligned} [\text{Ca}^{2+}] &= 2.05 \times 10^{-4} + 1.53 \times 10^{-5} \text{ mol L}^{-1} = 2.20 \times 10^{-4} \text{ mol L}^{-1} \\ [\text{CO}_3^{2-}] &= 1.53 \times 10^{-5} \text{ mol L}^{-1} \end{aligned}$$

If the initial calcium concentration had been zero, K_{sp} equation would have given

$$\begin{aligned} K_{sp} &= [\text{Ca}^{2+}][\text{CO}_3^{2-}] = x^2 = 3.36 \times 10^{-9} \\ x &= \sqrt{3.36 \times 10^{-9}} = 5.80 \times 10^{-5} \end{aligned}$$

In the absence of an initial calcium ion concentration, the extent of reaction (dissolution of calcium carbonate) is larger; 5.80×10^{-5} versus 1.53×10^{-5} . If the original solution contained neither calcium nor carbonate ions (e.g. a potassium bromide solution), then the dissolution of calcium carbonate would be unaffected.¹

¹ Actually, the presence of ions already in solution does have an affect on the dissolution of CaCO_3 . This is because concentrations are not good approximations for ions in solutions. We

Example 5.7: What is the extent of dissolution of AgCl(s) ($K_{sp} = 1.8 \times 10^{-10}$) in the following solutions when equilibrium is established? What are the equilibrium ion concentrations?

- (a) $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ KBr(aq)}$
 (b) $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ KCl(aq)}$

Approach: Construct ICE tables. Look for common ions. Substitute equilibrium concentrations into the solubility product and solve for the extent of reaction (extent of dissolution in this case).

In the first case, there are no initial common ions. In the second case, there are chloride ions already present.

(a) Initially, there are potassium and bromide ions present in solution, but no lead or chloride.

	AgCl(s)	\rightleftharpoons	$\text{Ag}^+(\text{aq})$	+	$\text{Cl}^-(\text{aq})$
Initial			0		0
Change			+ x		+ x
Equilibrium			x		x

Substitute the equilibrium ion concentrations into the solubility product equation.

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = x^2 = 1.8 \times 10^{-10}$$

which gives the extent of dissolution,

$$x = (1.8 \times 10^{-10})^{1/2} = 1.34 \times 10^{-5} \text{ mol L}^{-1}$$

At equilibrium,

$$[\text{Ag}^+] = [\text{Cl}^-] = x = 1.3 \times 10^{-5} \text{ mol L}^{-1}$$

(b) Initially, there is $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ Cl}^-(\text{aq})$ – a common ion – present in solution.

	AgCl(s)	\rightleftharpoons	$\text{Ag}^+(\text{aq})$	+	$\text{Cl}^-(\text{aq})$
Initial			0		1.0×10^{-3}
Change			+ x		+ x
Equilibrium			x		$1.0 \times 10^{-3} + x$

Substitute the equilibrium ion concentrations into the solubility product equation.

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (1.0 \times 10^{-3} + x)x = 1.8 \times 10^{-10}$$

must include a correction factor for each ion – the activity coefficient. The correction factor is different if there are already ions in solution, however we will not take this into account in Chem 1A03/1E03. A common ion has a much greater effect on solubility and we will take it into account.

which gives

$$x^2 + 1.0 \times 10^{-3}x - 1.8 \times 10^{-10} = 0$$

Using the quadratic formula,

$$\begin{aligned} x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ &= \frac{-1.0 \times 10^{-3} \pm \sqrt{(1.0 \times 10^{-3})^2 + 4 \times 1.8 \times 10^{-10}}}{2} \\ &= \begin{cases} 1.8_0 \times 10^{-7} \\ -1.0_0 \times 10^{-3} \end{cases} \end{aligned}$$

The negative solution produces a negative silver concentration at equilibrium and is therefore inadmissible. The extent of dissolution is therefore

$$x = 1.8 \times 10^{-7} \text{ mol L}^{-1}$$

At equilibrium,

$$\begin{aligned} [\text{Ag}^+] &= 1.8 \times 10^{-7} \text{ mol L}^{-1} \\ [\text{Cl}^-] &= 1.0 \times 10^{-3} + 1.8_0 \times 10^{-7} \text{ mol L}^{-1} = 1.0 \times 10^{-3} \text{ mol L}^{-1} \end{aligned}$$

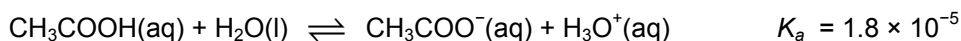
In this example, the extent of dissolution is reduced almost 100-fold when $1.0 \times 10^{-3} \text{ mol L}^{-1}$ is *already* present in solution. Note that the chloride ion concentration changes a negligible amount.

5.6 Acid base equilibrium

When the equilibrium corresponds to the dissociation of an acid, $\text{HA}(\text{aq})$, into $\text{H}^+(\text{aq})$ and $\text{A}^-(\text{aq})$, the equilibrium constant is called K_a . K_a determines the extent of dissociation of the acid and the resulting H^+ concentration (and pH). Note that H^+ is actually transferred to water making $\text{H}_3\text{O}^+(\text{aq})$. $\text{H}^+(\text{aq})$ is a convenient shorthand for $\text{H}_3\text{O}^+(\text{aq})$, that eliminates the need to carry an extra water on the reactant side of the equation.

Strong acids dissociate completely and do not require an equilibrium analysis.

Consider the dissociation of ethanoic acid, a *weak* acid.



The equilibrium concentrations for a 1.00 mol L^{-1} ethanoic acid solution are determined in the usual way, starting with an ICE table.

	$\text{CH}_3\text{COOH}(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{CH}_3\text{COO}^-(\text{aq})$	+	$\text{H}_3\text{O}^+(\text{aq})$
Initial	1.00				0		0
Change	$-x$				$+x$		$+x$
Equilibrium	$1.00 - x$				x		x

Substitute the equilibrium concentrations into the equilibrium constant expression. Note that the activity of $\text{H}_2\text{O}(\text{l})$ is 1 and does not appear in the K_a expression; pure liquids and solids do not appear in K expressions.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{1.00 - x} = 1.8 \times 10^{-5}$$

This equation can be rearranged to quadratic form,

$$x^2 + 1.8 \times 10^{-5}x - 1.8 \times 10^{-5} \times 1.00 = 0$$

with solution,

$$x = \frac{-1.8 \times 10^{-5} \pm \sqrt{(1.8 \times 10^{-5})^2 + 4 \times 1.8 \times 10^{-5} \times 1.00}}{2}$$

$$= \begin{cases} 4.2_3 \times 10^{-3} \\ -4.2_5 \times 10^{-3} \end{cases}$$

Only the positive solution is admissible. Therefore, the extent of dissociation is 4.2×10^{-3} and the equilibrium concentrations are given by

$$[\text{CH}_3\text{COOH}] = 1.00 - x = 0.99_6 \text{ mol L}^{-1} \approx 1.00 \text{ mol L}^{-1}$$

$$[\text{CH}_3\text{COO}^-] = [\text{H}_3\text{O}^+] = x = 4.2 \times 10^{-3} \text{ mol L}^{-1}$$

Note that the extent of reaction is very small compared to the initial concentration of CH_3COOH . In fact, the final concentration of CH_3COOH is the same within the accuracy of the given data. This suggests an approximation method for solving the equilibrium equation.

Neglect x (i.e., assume x is small and negligible) in the denominator of the above expression for K_a ; specifically, let $1.00 - x \approx 1.00$ (an excellent approximation in the current example). The equilibrium equation simplifies to

$$\frac{x^2}{1.00} = 1.8 \times 10^{-5}$$

$$x = \sqrt{1.8 \times 10^{-5} \times 1.00} = 4.2_4 \times 10^{-3}$$

The approximation gives the same extent of reaction as the quadratic formula, to within the accuracy of the given data.

Example 5.8: Use the approximation,

$$[\text{HA}]_{\text{eqm}} = [\text{HA}]_{\text{initial}} - x \approx [\text{HA}]_{\text{initial}}$$

to determine the pH of 2.00 mol L^{-1} solutions of

- (a) HF $K_a = 6.3 \times 10^{-4}$
- (b) HCN $K_a = 6.2 \times 10^{-10}$

(c) H_2S $K_{a1} = 8.9 \times 10^{-8}$

Approach: Set up ICE table as above. Substitute equilibrium concentrations into the expression for the equilibrium constant. Determine x using the approximation method.

(a)

	HF(aq)	+	$\text{H}_2\text{O(l)}$	\rightleftharpoons	$\text{F}^{\text{-(aq)}}$	+	$\text{H}_3\text{O}^{\text{+(aq)}}$
Initial	2.00				0		0
Change	$-x$				$+x$		$+x$
Equilibrium	$2.00 - x$				x		x

Substitute the equilibrium concentrations into the equilibrium constant.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{x^2}{2.00 - x} = 6.3 \times 10^{-4}$$

Upon invoking the approximation, $2.00 - x \approx 2.00$, this equation simplifies to

$$\frac{x^2}{2.00} = 6.3 \times 10^{-4}$$

$$x = \sqrt{6.3 \times 10^{-4} \times 2.00} = 3.5_5 \times 10^{-2}$$

Therefore,

$$[\text{H}_3\text{O}^+] = x = 3.5_5 \times 10^{-2} \text{ mol L}^{-1}$$

$$\text{pH} = -\log_{10}([\text{H}_3\text{O}^+]) = -\log_{10}(3.5_5 \times 10^{-2}) = 1.45$$

(b) The calculation is the same as in part (a) except that $K_a = 6.2 \times 10^{-10}$. Thus, the extent of reaction at equilibrium is given by

$$\frac{x^2}{2.00} = 6.2 \times 10^{-10}$$

$$x = \sqrt{6.2 \times 10^{-10} \times 2.00} = 3.5_2 \times 10^{-5}$$

Therefore,

$$[\text{H}_3\text{O}^+] = x = 3.5_2 \times 10^{-5} \text{ mol L}^{-1}$$

$$\text{pH} = -\log_{10}([\text{H}_3\text{O}^+]) = -\log_{10}(3.5_2 \times 10^{-5}) = 4.45$$

(c) Here, we have

$$x = \sqrt{8.9 \times 10^{-8} \times 2.00} = 4.2_2 \times 10^{-4}$$

and

$$[\text{H}_3\text{O}^+] = x = 4.2_2 \times 10^{-4} \text{ mol L}^{-1}$$

$$\text{pH} = -\log_{10}([\text{H}_3\text{O}^+]) = -\log_{10}(4.2_2 \times 10^{-4}) = 3.37$$

How do we know when the acid is sufficiently concentrated to permit use of the above approximation? There is a rule based on the requirement that x be no more than $[\text{HA}]_{\text{initial}}/10$. Since $x \cong \sqrt{K_a[\text{HA}]_{\text{initial}}}$ (the approximation is good enough for this purpose), the rule takes the form,

$$\sqrt{K_a[\text{HA}]_{\text{initial}}} < \frac{[\text{HA}]_{\text{initial}}}{10}$$

or

$$\sqrt{\frac{[\text{HA}]_{\text{initial}}}{K_a}} > 10$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} > 100$$

If the initial HA concentration is too small ($<100 K_a$), we must solve the quadratic equation.

Example 5.9: What is the pH of a $1.00 \times 10^{-3} \text{ mol L}^{-1}$ solution of formic acid, $\text{HCOOH}(\text{aq})$ ($K_a = 1.8 \times 10^{-4}$)?

Approach: Set up the ICE table. Substitute equilibrium concentrations into expression for the equilibrium constant. Solve for the extent of reaction. Determine $[\text{H}_3\text{O}^+]$ and pH.

In this case, the initial HA concentration is less than 6 times bigger than K_a . We must solve the quadratic equation.

	$\text{HCOOH}(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{HCOO}^-(\text{aq})$	+	$\text{H}_3\text{O}^+(\text{aq})$
Initial	1.00×10^{-3}				0		0
Change	$-x$				$+x$		$+x$
Equilibrium	$1.00 \times 10^{-3} - x$				x		x

Substitute the equilibrium concentrations into the equilibrium constant.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{x^2}{1.00 \times 10^{-3} - x} = 1.8 \times 10^{-4}$$

This equation is rearranged to quadratic form,

$$x^2 + 1.8 \times 10^{-4}x - 1.8 \times 10^{-4} \times 1.00 \times 10^{-3} = 0$$

with solution,

$$x = \frac{-1.8 \times 10^{-4} \pm \sqrt{(1.8 \times 10^{-4})^2 + 4 \times 1.8 \times 10^{-4} \times 1.00 \times 10^{-3}}}{2}$$

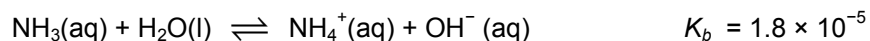
$$= \begin{cases} 3.4_4 \times 10^{-4} \\ -5.2_4 \times 10^{-4} \end{cases}$$

Only the positive solution is admissible. Therefore, the extent of dissociation is 3.4×10^{-4} and the equilibrium concentrations are given by

$$[\text{HCOOH}] = 1.00 \times 10^{-3} - x = 1.00 \times 10^{-3} - 3.4 \times 10^{-4} = 0.66 \text{ mol L}^{-1}$$

$$[\text{HCOO}^-] = [\text{H}_3\text{O}^+] = x = 3.4 \times 10^{-4} \text{ mol L}^{-1}$$

Weak bases can be treated in exactly the same fashion as weak acids. The equilibrium constant for the reaction of a base with water to form OH^- is called K_b . For example,



Example 5.10: What is the pH of a (a) 1.00 mol L^{-1} and (b) $1.00 \times 10^{-3} \text{ mol L}^{-1}$ solution of ammonia, $\text{NH}_3(\text{aq})$?

Approach: Exactly like a weak acid calculation, except that B replaces HA, HB^+ replaces A^- and OH^- replaces H_3O^+ .

(a)

	$\text{NH}_3(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{NH}_4^+(\text{aq})$	$\text{OH}^-(\text{aq})$
Initial	1.00				0	0
Change	$-x$				$+x$	$+x$
Equilibrium	$1.00 - x$				x	x

Substitute the equilibrium concentrations into the equilibrium constant.

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{1.00 - x} = 1.8 \times 10^{-5}$$

The approximation, $1.00 - x \approx 1.00$ is good here. Therefore,

$$x^2 = 1.8 \times 10^{-5} \times 1.00$$

$$x = \sqrt{1.8 \times 10^{-5}} = 4.2_4 \times 10^{-3}$$

Therefore,

$$[\text{OH}^-] = x = 4.2_4 \times 10^{-3} \text{ mol L}^{-1}$$

$$\text{pOH} = -\log_{10}([\text{OH}^-]) = -\log_{10}(4.2_4 \times 10^{-3}) = 2.37$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.37 = 11.63$$

(b)

	$\text{NH}_3(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{NH}_4^+(\text{aq})$	+	$\text{OH}^-(\text{aq})$
Initial	1.00×10^{-3}				0		0
Change	$-x$				$+x$		$+x$
Equilibrium	$1.00 \times 10^{-3} - x$				x		x

Substitute the equilibrium concentrations into the equilibrium constant.

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{1.00 \times 10^{-3} - x} = 1.8 \times 10^{-5}$$

The solution is dilute, thus $1.00 \times 10^{-3} - x$ cannot be approximated. The equation is rearranged to quadratic form,

$$x^2 + 1.8 \times 10^{-5}x - 1.8 \times 10^{-5} \times 1.00 \times 10^{-3} = 0$$

with solution,

$$x = \frac{-1.8 \times 10^{-5} \pm \sqrt{(1.8 \times 10^{-5})^2 + 4 \times 1.8 \times 10^{-5} \times 1.00 \times 10^{-3}}}{2}$$

$$= \begin{cases} 1.2_5 \times 10^{-4} \\ -1.4_3 \times 10^{-4} \end{cases}$$

The admissible solution ($x = 1.2_5 \times 10^{-4}$) gives

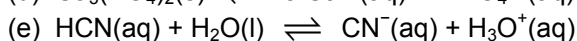
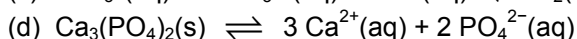
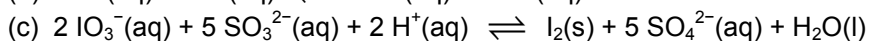
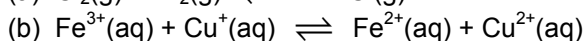
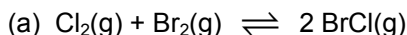
$$[\text{OH}^-] = x = 1.2_5 \times 10^{-4} \text{ mol L}^{-1}$$

$$\text{pOH} = -\log_{10}([\text{OH}^-]) = -\log_{10}(1.2_5 \times 10^{-4}) = 3.90$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.90 = 10.10$$

Problems:

5.1 Write down expressions for the equilibrium constants of the following reactions, in terms of equilibrium concentrations and/or partial pressures.



- 5.2 An equilibrium mixture of N_2O_4 and NO_2 , at 25°C , has a N_2O_4 partial pressure of 2.00 atm. What is the partial pressure of NO_2 ?



- 5.3 Write down the equilibrium constants for the following reactions given the data table of equilibrium constants below.

- (a) $\text{Fe}^{3+}(\text{aq}) + \text{Cu}^+(\text{aq}) \rightleftharpoons \text{Fe}^{2+}(\text{aq}) + \text{Cu}^{2+}(\text{aq})$
 (b) $2 \text{Fe}^{2+}(\text{aq}) + \text{Cl}_2(\text{aq}) \rightleftharpoons 2 \text{Fe}^{3+}(\text{aq}) + 2 \text{Cl}^-(\text{aq})$
 (c) $2 \text{NaF}(\text{s}) + \text{Mg}^{2+}(\text{aq}) \rightleftharpoons \text{MgF}_2(\text{s}) + 2 \text{Na}^+(\text{aq})$

DATA:

Reaction	Equilibrium Constant
1) $2 \text{Fe}^{3+}(\text{aq}) + \text{Cl}_2(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) \rightleftharpoons 2 \text{Fe}^{2+}(\text{aq}) + 2 \text{HOCl}(\text{aq}) + 2 \text{H}^+(\text{aq})$	K_1
2) $2 \text{HOCl}(\text{aq}) + 2 \text{Cu}^+(\text{aq}) + 2 \text{H}^+(\text{aq}) \rightleftharpoons \text{Cl}_2(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) + 2 \text{Cu}^{2+}(\text{aq})$	K_2
3) $2 \text{Cu}^+(\text{aq}) + \text{Cl}_2(\text{aq}) \rightleftharpoons 2 \text{Cu}^{2+}(\text{aq}) + 2 \text{Cl}^-(\text{aq})$	K_3
4) $\text{MgF}_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2 \text{F}^-(\text{aq})$	K_4
5) $\text{NaF}(\text{s}) \rightleftharpoons \text{Na}^+(\text{aq}) + \text{F}^-(\text{aq})$	K_5

- 5.4 Predict the direction each of the following equilibria shifts when the indicated changes are imposed.

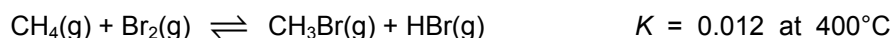


- (a) The N_2O_4 partial pressure is increased
 (b) Some NO_2 is removed from the reaction mixture
 (c) The reaction mixture is transferred to a vessel with twice the volume
 (d) Temperature is increased



- (e) Some KF is dissolved in the solution
 (f) Some solid MgF_2 is added to the mixture
 (g) Temperature is decreased

- 5.5 Determine the equilibrium partial pressure of all gases in the following equilibrium, after a vessel is prepared at 400°C with 10.0 atm partial pressure of both methane and bromine.



- 5.6 (a) What is the extent of dissolution of $\text{Ba}_3(\text{PO}_4)_2(\text{s})$ ($K_{\text{sp}} = 3.4 \times 10^{-23}$), and the equilibrium ion concentrations, in a $1.0 \times 10^{-5} \text{ mol L}^{-1}$ $\text{KBr}(\text{aq})$ solution?
 (b) How would the extent of dissolution of $\text{Ba}_3(\text{PO}_4)_2(\text{s})$ be different in a $1.0 \times 10^{-5} \text{ mol L}^{-1}$ $\text{K}_3\text{PO}_4(\text{aq})$ solution? (Just answer qualitatively – no calculations required.)
- 5.7 What is the pH of a (a) 1.00 mol L^{-1} and (b) $1.00 \times 10^{-6} \text{ mol L}^{-1}$ solution of hypochlorous acid? $K_{\text{a}}(\text{HOCl}) = 4.0 \times 10^{-8}$

5.8 What is the pH of a (a) 1.00 mol L^{-1} and (b) $1.00 \times 10^{-3} \text{ mol L}^{-1}$ solution of ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$? $K_b(\text{CH}_3\text{CH}_2\text{NH}_2) = 4.5 \times 10^{-4}$