Equilibrium

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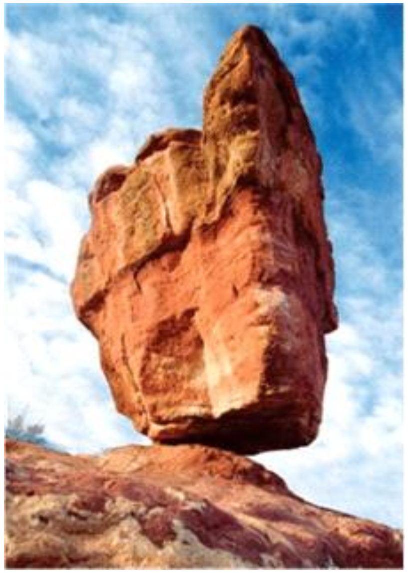
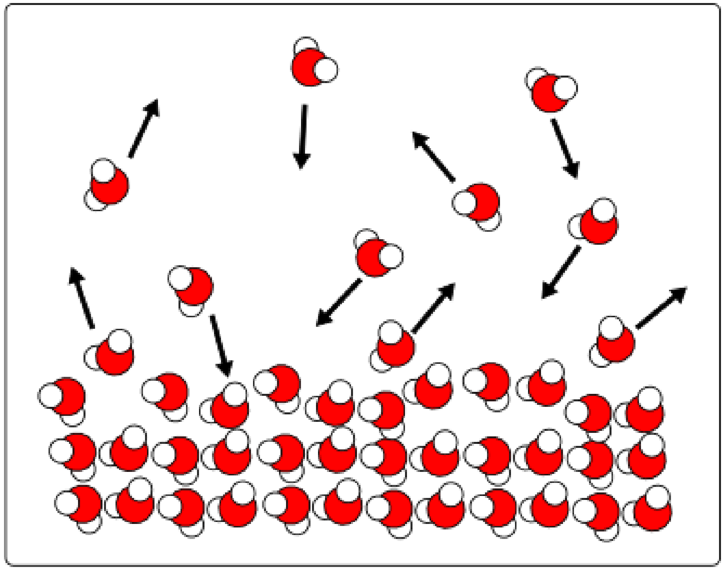
What is equilibrium?

Equilibrium is a state of balance between opposing forces or actions that is either static (as in a body acted on by forces whose resultant is zero) or dynamic (as in a reversible chemical reaction when the rates of reaction in both directions are equal)

– Merriam-Webster online dictionary



Static equilibrium
(more relevant to mechanics)



Dynamic equilibrium
(more relevant to chemistry)

Examples of chemical equilibria

$H_2O(\ell) \rightleftharpoons H_2O(g)$ (equilibrium vapor pressure)

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ (decomposition of a solid)

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ (solubility product)

$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$ (decomposition of a gas)

$H_2O(\ell) \rightleftharpoons H^+(aq) + OH^-(aq)$ (dissociation of a weak acid)

C_6H_5COOH (in ether solution) $\rightleftharpoons C_6H_5COOH$ (aq)

(benzoic acid – partitioning between two immiscible liquid phases)

In all cases, this is a dynamic equilibrium, with reactant molecules becoming products, and products becoming reactants.

Le Châtelier's Principle

Probably the most general qualitative description of equilibrium that has ever been articulated.

"When a system at equilibrium is subjected to change in concentration, temperature, volume, or pressure, then the system readjusts itself to (partially) counteract the effect of the applied change and a new equilibrium is established."

Example: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ + heat (ΔH = -92 kJ/mol)

4 molar volumes ↑ (reactants) 2 molar volumes ↑ (products)

Decreasing the volume → More NH_3 is produced

Adding N_2 or H_2 → More NH_3 is produced

Adding heat (increasing T) → NH_3 is converted to N_2 + and H_2

NH_3 is added → NH_3 is converted to N_2 + and H_2

Kinetic model for equilibrium

In a dynamic equilibrium, the forward and reverse rates must be equal. Thus, for the reaction

$$aA + bB \rightleftharpoons cC + dD,$$

at equilibrium the rate of the forward reaction $aA + bB \longrightarrow cC + dD$

must equal the rate of the reverse reaction $aA + bB \longleftarrow cC + dD$

In 1865, Cato Maximillian Guldberg and Peter Waage proposed that the rates of the forward and reverse reactions are given by

$$\text{Forward reaction rate} = k_+ [A]^a[B]^b$$

$$\text{Reverse reaction rate} = k_- [C]^c[D]^d$$

Here [A] is the concentration of species A, *etc.*, and the powers *a, b, …* are the stoichiometric coefficients. For gases, partial pressures, P_A, P_B, *etc.* may be used, instead.

At equilibrium, the two rates must be equal, so $k_+ [A]^a[B]^b = k_- [C]^c[D]^d$. This can be arranged to give

$$K = \frac{k_+}{k_-} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$, where K is called the equilibrium constant.

REMEMBER: Products are in the numerator, reactants in the denominator!

Problems with the kinetic model

Although there is strong experimental support for the result of the kinetic model that

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

is a constant, there are now many reactions known that do not obey the rate laws proposed by Guldberg and Waage.

Examples:

$2N_2O_5(g) \longrightarrow N_2O_4(g) + O_2(g)$ Rate = $k[N_2O_5]$, NOT $k[N_2O_5]^2$

$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$ Rate = $\frac{k[H_2][Br_2]^{1/2}}{1+k'[HBr]/[Br_2]}$, NOT $k[H_2][Br_2]$

These reactions don't follow the simple rate law that one would expect, because they proceed through a series of intermediate steps. They're not simple, direct, one-step reactions. Still, the equilibrium constant expression given above remains valid.

Thermodynamic model for equilibrium

Let's start with the Gibbs free energy of an ideal gas. We can define the Gibbs free energy of one mole of gas at a certain temperature and one atmosphere of pressure as the standard molar Gibbs free energy of the substance, symbolized by G°(T). If we want to know the Gibbs free energy at some different pressure, we need to know that the Gibbs free energy changes with pressure according to:

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

Imagine starting at the standard state (one atmosphere) and changing the pressure of the gas. Then, the Gibbs free energy at a different pressure is

$$G(T,P) = G°(T) + \int_{1\,atm}^{p} \left(\frac{\partial G}{\partial p}\right)_T dp = G°(T) + \int_{1\,atm}^{p} V\,dp$$

For an ideal gas, $pV = nRT$, so $V = \frac{nRT}{p}$ (but for one mole, $n = 1$) so

$$G(T,P) = G°(T) + \int_{1\,atm}^{p} \frac{RT}{p} dp$$

$$\boxed{G(T,P) = G°(T) + RT\,ln\frac{p}{1\,atm}}$$

At equilibrium, ΔG = 0.

For the gas-phase reaction,

$$aA + bB \rightleftharpoons cC + dD,$$

the value of ΔG is

$$\Delta G = cG_C(T,P) + dG_D(T,P) - aG_A(T,P) - bG_B(T,P)$$

This accounts for the fact that we have *a* moles of reactant A, etc.

Using the previous result that

$$G(T,P) = G°(T) + RT\ ln\frac{p}{1\ atm}\ ,$$

Therefore, $\Delta G(T,P) = cG_C\ °(T) + cRT\ ln\frac{p_C}{1\ atm} + dG_D\ °(T) + dRT\ ln\frac{p_D}{1\ atm}$

$$-aG_A\ °(T) -\ aRT\ ln\frac{p_A}{1\ atm} - bG_B\ °(T) - bRT\ ln\frac{p_B}{1\ atm}$$

Letting $\Delta G°(T) \equiv cG_C\ °(T) + dG_D\ °(T) - aG_A\ °(T) - bG_B\ °(T)$ and rearranging the logarithms gives

$$\Delta G(T,P) = \Delta G°(T) + RT\ ln\frac{\left(\frac{p_C}{1\ atm}\right)^c\left(\frac{p_D}{1\ atm}\right)^d}{\left(\frac{p_A}{1\ atm}\right)^a\left(\frac{p_B}{1\ atm}\right)^b}$$

Because $\Delta G(T,P)$= 0 at equilibrium, this gives $\Delta G°(T) = -\ RT\ ln\frac{\left(\frac{p_C}{1\ atm}\right)^c\left(\frac{p_D}{1\ atm}\right)^d}{\left(\frac{p_A}{1\ atm}\right)^a\left(\frac{p_B}{1\ atm}\right)^b}$.

The equilibrium constant, K

If we're careful to always measure pressure in units of the defined standard state (atmospheres), then this can be simplified to:

$$\Delta G°(T) = -RT\,ln\frac{(p_C)^c(p_D)^d}{(p_A)^a(p_B)^b}$$

Solving for the pressure ratio term:

$$\frac{(p_C)^c(p_D)^d}{(p_A)^a(p_B)^b} = e^{-\frac{\Delta G°(T)}{RT}}$$

At a specific temperature, the right hand side takes on a specific value, which we can call K, the equilibrium constant:

$$\frac{(p_C)^c(p_D)^d}{(p_A)^a(p_B)^b} = K$$

And K follows the equation $\boxed{\Delta G°(T) = -RT\,lnK}$ or $\boxed{K = e^{-\frac{\Delta G°(T)}{RT}}}$

Of course, real gases do not follow pV = RT precisely (one mole is assumed). Corrections to the equilibrium constant expression are made by using the fugacity of the gas, instead of the pressure in the equilibrium expression.

Solutions

A similar result is obtained for the solution phase reaction

$$aA + bB \rightleftharpoons cC + dD,$$

Where the standard reference state is a 1 M solution. This gives a ΔG for the reaction occurring at different concentrations as

$$\Delta G(T,P) = \Delta G°(T) + RT\ ln\frac{\left(\frac{[C]}{1\ M}\right)^c\left(\frac{[D]}{1\ M}\right)^d}{\left(\frac{[A]}{1\ M}\right)^a\left(\frac{[B]}{1\ M}\right)^b}$$

At equilibrium, ΔG=0; if we also reference the concentrations to the standard state (1M), we get

$$\Delta G°(T) = -\ RT\ ln\frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{or} \quad \frac{[C]^c[D]^d}{[A]^a[B]^b} = \ e^{-\frac{\Delta G°(T)}{RT}}$$

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

And K again follows the equations $\boxed{\Delta G°(T) = -\ RT\ lnK}$ or $\boxed{K = \ e^{-\frac{\Delta G°(T)}{RT}}}$

Again, corrections for nonideal behavior are needed if the concentrations are too high; then activities instead of concentrations must be used.

What's the Point?

Equilibrium and equilibrium constants come from thermodynamics – NOT from kinetics.

In some cases (beyond AP Chemistry) it may be necessary to correct gas pressures to fugacities and solution concentrations to activities to obtain valid results.

Temperature Dependence

Regardless of whether we're dealing with gas-phase or solution equilibria, we have:

$\Delta G°(T) = -RT \ln K$ (Remember, R = gas constant = 8.314 J·mol^{-1}·K^{-1})

However, ΔG = ΔH – TΔS, so ΔG° = ΔH° – TΔS°. If we measure K over a range of temperatures, we get

$$\ln K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R}$$

A plot of $\ln K$ vs. $\frac{1}{T}$ will have a slope of $-\frac{\Delta H°}{R}$ and a y-intercept of $\frac{\Delta S°}{R}$. This is called a van't Hoff plot, after J. H. van't Hoff (a Dutch chemist, 1884).

The equation can also be differentiated with respect to T, giving

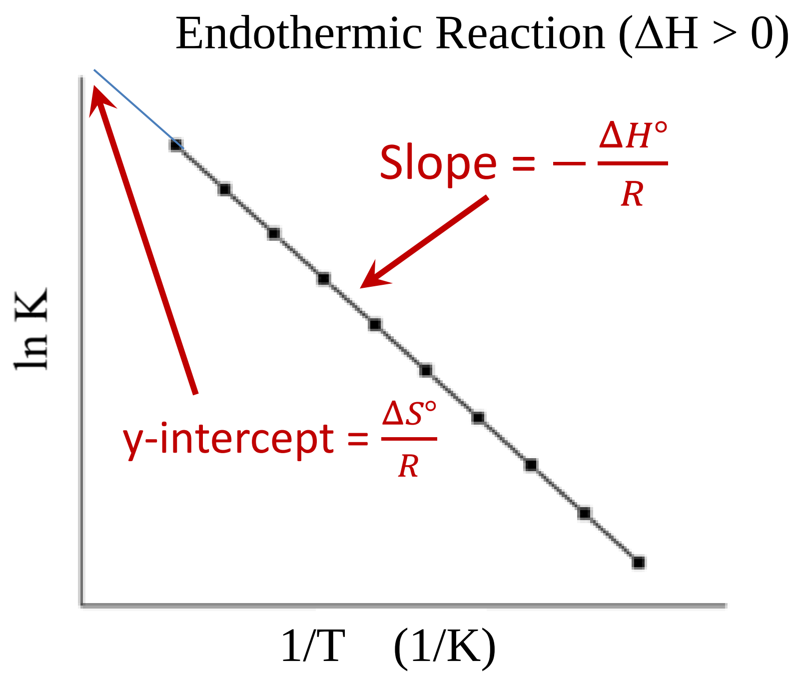
$$\frac{d \ln K}{dT} = \frac{\Delta H°}{RT^2}$$ (the van't Hoff equation)

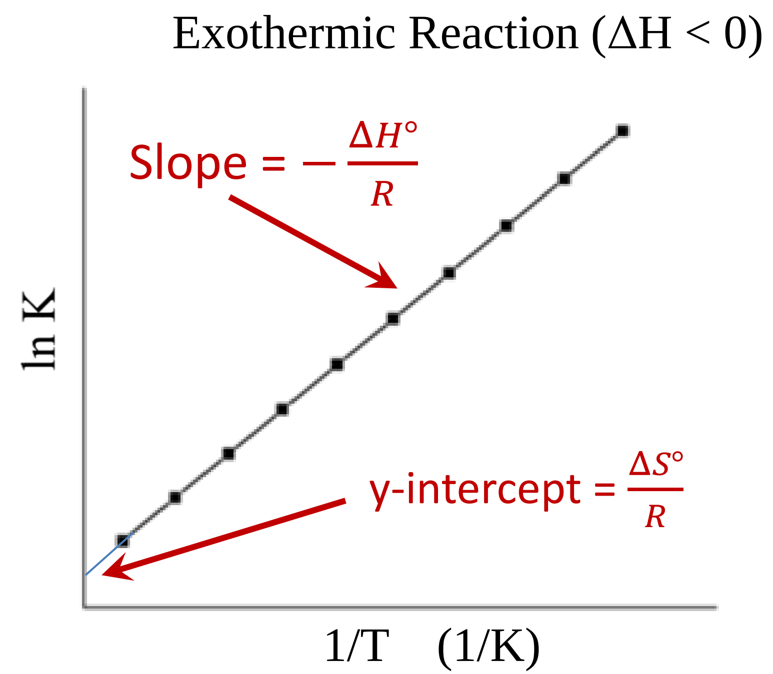
Another useful expression coming from the first equation is

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

In all cases this assumes that ΔH° and ΔS° are independent of T. This is never precisely true, and is on rare occasions a significant error.

Examples of van’t Hoff plots





From: https://en.wikipedia.org/wiki/Van_%27t_Hoff_equation

A common mistake: Failure to measure T in Kelvins!

A note on solids and liquids

If an equilibrium involves a pure solid or a liquid, as in:

$H_2O(\ell) \rightleftharpoons H_2O(g)$ (equilibrium vapor pressure)

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ (decomposition of a solid)

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ (solubility product)

$H_2O(\ell) \rightleftharpoons H^+(aq) + OH^-(aq)$ (dissociation of water)

$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ (hydrolysis of a weak base)

Then, the activity of the pure substance is constant. It isn't necessary to include this as a variable in the equilibrium constant expression, so it is dropped. This is possible because the substance is already in its standard state. Therefore, we write the equilibrium expressions as:

$H_2O(\ell) \rightleftharpoons H_2O(g)$ $K = P(H_2O)$ (equilibrium vapor pressure)

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $K = P(CO_2)$ (also, an equilibrium vapor pressure)

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ $K = [Ag^+][Cl^-]$ (solubility product)

$H_2O(\ell) \rightleftharpoons H^+(aq) + OH^-(aq)$ $K_w = [H^+][OH^-]$

etc.

Now, let's solve some problems!

The Haber synthesis of NH_3

For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $K_p = 1.45 \times 10^{-5}$ at 500°C. If an equilibrium mixture at this temperature has partial pressures of 0.928 atm for H_2 and 0.432 atm for N_2, what is the partial pressure of NH_3 in the mixture?

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First, the standard state of the gases is 1 atm, so K_p is calculated in atm.

$$\frac{{p_{NH_3}}^2}{p_{N_2}p_{H_2}^3} = 1.45 \times 10^{-5}$$

$$\frac{{p_{NH_3}}^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}$$

$${p_{NH_3}}^2 = (1.45 \times 10^{-5})(0.432)(0.928)^3 = 5.01 \times 10^{-6}$$

$$p_{NH_3} = \sqrt{5.01 \times 10^{-6}} = \boxed{2.24 \times 10^{-3}\ atm}$$

QUESTION: How would this change if the partial pressures of H_2 and N_2 were 10 times larger (9.28 atm H_2 and 4.32 atm N_2)?

The Haber synthesis of NH_3

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ANSWER: Since both were multiplied by 10, the denominator is multiplied by 10^4. The numerator must also be multiplied by 10^4, so p_{NH_3} must be multiplied by 10^2, giving

$$p_{NH_3} = \boxed{2.24 \times 10^{-3} atm \times 10^2 = 0.224\ atm}$$

The Haber synthesis of NH_3

A more complicated problem: If a vessel is filled to partial pressures of 1 atm N_2 and 3 atm H_2, sealed, and heated to 500°C, what partial pressure of NH_3 is obtained?

[Remember: $K_p = 1.45 \times 10^{-5}$ at 500°C]

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

This is a problem that can be solved using an ICE table (Initial, Change, Equilibrium):

	N_2	H_2	NH_3
Initial	1	3	0
Change	-x	-3x	2x
Equilibrium	1-x	3-3x	2x

$$\frac{{p_{NH_3}}^2}{p_{N_2} p_{H_2}^3} = \frac{(2x)^2}{(1-x)(3-3x)^3} = 1.45 \times 10^{-5}$$

If we multiply this out, we'll get a 4^{th}-order polynomial equation that will be next to impossible to solve. We need an approximate method that will be accurate. The key is to recognize that because the equilibrium constant is so small, x will be small.

This sort of recognition is often the trick to simple solutions of equilibrium problems.

The Haber synthesis of NH_3

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$$\frac{{p_{NH_3}}^2}{p_{N_2} p_{H_2}^3} = \frac{(2x)^2}{(1-x)(3-3x)^3} = 1.45 \times 10^{-5}$$

Assume: x << 1, so we can neglect x in comparison to 1 in the denominator (and 3x in comparison to 3). This gives $\frac{(2x)^2}{(1)(3)^3} = 1.45 \times 10^{-5}$, or $\frac{4}{27}x^2 = 1.45 \times 10^{-5}$, or $x^2 = 9.79 \times 10^{-5}$

$$\therefore x = 9.89 \times 10^{-3} = 0.00989\ atm \quad p_{NH_3} = 2x = \boxed{0.0198\ atm}$$

The assumption that x ≪ 1 was justified. Otherwise, this is a difficult problem to solve (the algebra gets really messy, best solved by a series of approximations).

The Haber synthesis of NH_3

Yet another kind of problem: If a vessel is filled to partial pressures of 10.0 atm N_2, 30.0 atm H_2, and 5.00 atm NH_3 sealed, and equilibrated at 500°C, will the partial pressure of NH_3 rise or fall?

The Haber synthesis of NH_3

Yet another kind of problem: If a vessel is filled to partial pressures of 10 atm N_2, 30 atm H_2, and 5 atm NH_3 sealed, and equilibrated at 500°C, will the partial pressure of NH_3 rise or fall?

Solution: Calculate the reaction quotient, Q_p. This is the same expression as the equilibrium constant, but using the initial values of the partial pressures (or concentrations for a solution phase problem).

$$Q_p = \frac{{p_{NH_3}}^2}{p_{N_2} p_{H_2}^3} \text{ (calculated using initial values)}$$

$$Q_p = \frac{(5.00)^2}{(10.0)(30.0)^3} = 9.26 \times 10^{-5}$$

This is larger than K_p for this reaction, which is 1.45×10^{-5}. Therefore, the partial pressure of the product, NH_3, is too high (or the partial pressure of the reactants is too small). Either way, the reaction will proceed toward the reactants.

IN GENERAL:

If Q > K, the reaction will proceed toward reactants.

If Q < K, the reaction will proceed toward products.

Solubility Products

Many sparingly soluble salts exist, for which the equilibrium constant is of the form:

$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$ $K_{sp} = [Ag^{+}][Cl^{-}] = 1.7 \times 10^{-10}$

QUESTION: If 10.0g of AgCl are added to 1.00 L of pure water, how many grams will dissolve?

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QUESTION: If 10.0g of AgCl are added to 1.00 L of pure water, how many grams will dissolve?

ANSWER: In this case, equal amounts of Ag^{+} and Cl^{-} are released, so letting $x=[Ag^{+}]=[Cl^{-}]$, we get $x^2 = 1.7 \times 10^{-10}$, or $x = 1.30 \times 10^{-5}$ M.

Since we have 1.00L, this means 1.30×10^{-5} mol AgCl will dissolve, or $1.30 \times 10^{-5}\ mol \times \frac{143.2\ g}{1\ mol} = 1.87 \times 10^{-3}\ g = \boxed{1.87\ mg}$

The amount that dissolves is far less than the amount added to the solution, so it looks like none dissolved.

Solubility Products

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ $K_{sp} = [Ag^+][Cl^-] = 1.7 \times 10^{-10}$

A bit trickier question: If 10.0g of AgCl are added to 1.00 L of a 1.00 mM NaCl solution, how many grams will dissolve?

First: Will the amount that dissolves be greater than or less than the amount that dissolved in pure water?

Solubility Products

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = [Ag^+][Cl^-] = 1.7 \times 10^{-10}$$

A bit trickier question: If 10.0g of AgCl are added to 1.00 L of a 1.00 mM NaCl solution, how many grams will dissolve?

Answer: In this case, let's set up an ICE table (using molarity)

	Ag^+	Cl^-
Initial	0	0.001
Change	+x	+x
Equilibrium	x	0.001+x

$$K_{sp} = [Ag^+][Cl^-] = x(0.001+x) = 1.7 \times 10^{-10}.$$

Previously, we found in pure water a concentration of $[Ag^+]=[Cl^-]=1.30 \times 10^{-5}$ M was found, so we expect x to be much less than 0.001 (which is 1×10^{-3}). In the expression $x(0.001+x)= 1.7 \times 10^{-10}$, we can neglect x in comparison to 0.001, giving $x(0.001)= 1.7 \times 10^{-10}$, or $x= 1.7 \times 10^{-7}$ M.

For a 1.00 L volume, 1.7×10^{-7} mol AgCl $\left(\frac{143.2\ g}{1\ mol}\right)$=2.43×10-5 g = $\boxed{24.3\ \mu g}$

Addition of even a small amount of one of the ions greatly decreases the amount of AgCl dissolved. This is called the common ion effect.

Weak acids

Strong acids are acids that are said to dissociate completely, so the equilibrium $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$ lies far to the right.

For weak acids, the equilibrium lies far to the left, so that most of the acid molecules don't dissociate.

For $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$, the equilibrium constant is $K_a = \frac{[H^+][A^-]}{[HA]}$.

Strong acids: HI, HBr, $HClO_4$, HCl, $HClO_3$, H_2SO_4, and HNO_3 have K_a values of 10^{10} to 10^2, so a 1M solution of the acid has [HA] in the range of 10^{-10} to 10^{-2} M.

Weak acids have K_a values that are smaller than 10^{-2}. These may be compared using the pK_a values, where $pK_a \equiv -\log_{10}(K_a)$. [For example, if $K_a = 10^{-5}$, $pK_a=5$]

Common weak acids and pKa values:

Bisulfate ion or hydrogen sulfate ion	HSO_4^-	pKa = 1.92	$K_a = 1.2 \times 10^{-2}$
Phosphoric acid	H_3PO_4	pKa = 2.12	$K_a = 7.52 \times 10^{-3}$
Hydrofluoric acid	HF	pKa = 3.14	$K_a = 7.2 \times 10^{-4}$
Acetic acid	CH_3COOH	pKa = 4.75	$K_a = 1.76 \times 10^{-5}$
Carbonic acid	H_2CO_3	pKa = 6.37	$K_a = 4.3 \times 10^{-7}$

Weak acids

Problem: An 0.1 M solution of acetic acid is prepared. What is the pH of this solution?

Abbreviating: Acetic acid = CH_3COOH = HOAc Acetate ion = CH_3COO^- = OAc^-

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ K_a= 1.76 x 10^{-5}

	HOAc	H^+	OAc^-
Initial	0.1	0	0
Change	-x	x	X
Equilibrium	0.1-x	x	X

$$\frac{x^2}{0.1-x} = 1.76 \times 10^{-5}$$

Hard way:

$$x^2 + 1.76 \times 10^{-5}\, x - 1.76 \times 10^{-6} = 0$$

Quadratic formula gives x= 1.31788 x 10^{-3}

pH = -$\log_{10}$(1.31788 x 10^{-3}) = 2.880

Easy way:

x << 0.1, so replace 0.1-x with 0.1

$$\frac{x^2}{0.1} = 1.76 \times 10^{-5}$$

$$x^2 = 1.76 \times 10^{-6}$$

x = 1.3266 x 10^{-3} M

pH = -$\log_{10}$(1.3266 x 10^{-3})

pH = 2.877

Weak acids

Problem: A solution is prepared by adding 0.05 moles of acetic acid and 0.05 moles of sodium acetate to enough water to make up one liter of solution. What is the pH of this solution?

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ $K_a = 1.76 \times 10^{-5}$

	HOAc	H^+	OAc^-
Initial	0.05	0	0.05
Change	-x	x	x
Equilibrium	0.05-x	x	0.05+x

$$\frac{x(0.05+x)}{0.05-x} = 1.76 \times 10^{-5}$$

Hard way:

$$\frac{x(0.05+x)}{0.05-x} = 1.76 \times 10^{-5}$$

$$x^2 + 0.0500176\,x - 8.80 \times 10^{-8} = 0$$

Using quadratic formula: $x = 1.7588 \times 10^{-5}$ M

pH = 4.7548

Easy way:

This is a weak acid, so x << 0.05

$$\frac{x(0.05)}{0.05} = 1.76 \times 10^{-5}$$

$x = 1.76 \times 10^{-5}$ M

pH = 4.7545

Buffer solutions

We found that when we made a solution that was 0.05M in HOAc and 0.05M in NaOAc, our ICE table showed:

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^- \quad K_a = 1.76 \times 10^{-5}$$

	HOAc	H^+	OAc^-
Initial	0.05	0	0.05
Change	-x	x	x
Equilibrium	0.05-x	x	0.05+x

$$\frac{x(0.05+x)}{0.05-x} = 1.76 \times 10^{-5}$$

More generally, when a weak acid and its conjugate base are mixed, we get an equilibrium expression of:

$$\frac{x([A^-]_{initial}+x)}{[HA]_{initial}-x} = K_a$$

Because x is small compared to the initial concentrations, this gives

$$x = \frac{[HA]_{initial}}{[A^-]_{initial}} K_a \quad \text{and} \quad \boxed{pH = \log \frac{[HA]_{initial}}{[A^-]_{initial}} + pK_a}$$

Simplify equilibrium problems by finding equivalent systems

Problem: A solution is prepared by adding 0.10 moles of acetic acid and 0.05 moles of sodium hydroxide to enough water to make up one liter of solution. What is the pH of this solution?

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$

But we don't know the equilibrium constant, K, for this reaction! (We could figure it out using $K_w = [OH^-][H^+] = 10^{-14}$, to find $K = K_w K_a$.)

HOWEVER, OH^- is a strong base that will convert essentially all acetic acid to acetate!

The problem is equivalent to 0.05 moles of acetic acid and 0.05 moles of sodium acetate, dissolved in water to make 1.0 L of solution.

That was the last problem, which gave pH= 4.75.

Weak acids

Problem: What is the pH of an 0.1 M solution of sodium acetate?

Now we really do need to worry about the reaction

$$H_2O + CH_3COO^- \rightleftharpoons CH_3COOH + OH^- \qquad K = \frac{[HOAc][OH^-]}{[OAc^-]}$$

But we don't know K!

What we know: For $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$, $K_a = \frac{[H^+][OAc^-]}{[HOAc]} = 1.76 \times 10^{-5}$

Comparing the K we want, and the K_a we have, if we invert K_a, we'll be partly there.

$$\frac{[HOAc]}{[H^+][OAc^-]} = 5.68 \times 10^4$$

This places [HOAc] and $[OAc^-]$ where we want them.

Now if we multiply by $K_w = [OH^-][H^+] = 10^{-14}$ we get what we want:

$$\frac{[HOAc][H^+][OH^-]}{[H^+][OAc^-]} = 5.68 \times 10^4 \times 10^{-14}$$

$$\boxed{\frac{[HOAc][OH^-]}{[OAc^-]} = 5.68 \times 10^{-10}}$$

Now we have what we need to solve this problem.

Weak acids

Problem: What is the pH of an 0.1 M solution of sodium acetate?

Now we really do need to worry about the reaction

$H_2O + CH_3COO^- \rightleftharpoons CH_3COOH + OH^-$ $$K = \frac{[HOAc][OH^-]}{[OAc^-]} = 5.68 \times 10^{-10}$$

ICE TABLE:

	CH_3COO^-	CH_3COOH	OH^-
Initial	0.1	0	0
Change	-x	x	x
Equilibrium	0.1-x	x	x

$$\frac{x^2}{0.1-x} = 5.68 \times 10^{-10}$$

Again, x will be very small, so we may approximate 0.1-x ≈ 0.1.

$$x^2 = 5.68 \times 10^{-10} \times 0.1 = 5.68 \times 10^{-11}$$

$x = 7.54 \times 10^{-6} = [OH^-]$

pOH = -log(7.54×10^{-6}) = 5.123

pH = 14.0-pOH = **8.88 = pH**

The following reaction has K = 2. Which image shows the reaction at equilibrium?