CHM 1200 General Chemistry 2

You are responsible for remembering and being able to use EVERYTHING from CHM 1100. CHM 1200 is impossible to understand without the knowledge from CHM 1100. If you do not remember CHM 1100, you must review it immediately.

We will be doing even more Math than in CHM 1100. Have your scientific calculator ready!

Chapter 13: Kinetics

Kinetics means the rate of a chemical reaction – how fast is it.

It is perfectly possible to directly measure the rate of any reaction yourself by going into a lab, and running the reaction while timing it.

The REACTION RATE for a chemical is measured as the change of the amount of each chemical in a reaction over time. The RATE EXPRESSION normalizes the rates of all the chemicals through the stoichiometric mole ratio:

$$\text{Ex:} \quad 2\ NO_{(g)} + O_{2\ (g)} \longrightarrow 2\ NO_{2\ (g)}$$

$$rate = -\frac{1}{2}\frac{\Delta[NO]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = +\frac{1}{2}\frac{\Delta[NO_2]}{\Delta t}$$

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the rate law

However, measuring reactions over and over again is not necessary. It is possible to determine rate with a paper-and-pencil calculation. Reactions have a RATE LAW. A rate law always looks like:

$$rate = k\,[NO]^x\,[O_2]^y$$

Notice, the rate law has three parts:

(1) the reactant concentrations only (product rate is simple to determine from the rate expression)
(2) the rate constant - k - that depends on temperature; and
(3) the rate orders - exponents

Obviously, the reactants are just copied from the chemical equation. However, determining the rate constant and rate orders requires analyzing experimental data, by using a ratio method.

The rate orders can be almost any number in real Chemistry, but in this class, the rate orders are zero (0), one (1) or two (2). If you don't have zero, one or two in your solution, you have something wrong.

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half-lives

There is an alternate version of the rate law, which I call the the "time equation". It's officially called the integrated rate law, but I don't like this name, because it can be confused with the regular rate law, and because it hides what it is most useful for – calculating time values. How long does it take to run a reaction?

The most important time value is the half-life – the time required for exactly one-half of the reactant to react. Since half-life is a consistent measurement, it is a simple way to compare the rates of different reactions – the reaction with the shorter half-life is faster, or the reaction with the longer half-life is slower.

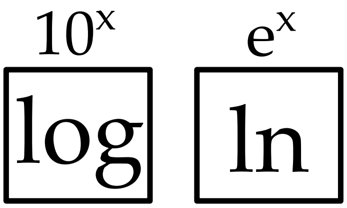
Be careful: the time equation, half-life formula and their graphs are distinct for zeroth, first and second-order reactions:

	zeroth order	first order	second order
equation	$A \longrightarrow B$	$A \longrightarrow B$	$A \longrightarrow B$
rate law	$rate = k$	$rate = k\,[A]$	$rate = k\,[A]^2$
time equation	$[A]_f = -kt + [A]_0$	$\ln [A]_f = -kt + \ln [A]_0$	$\frac{1}{[A]_f} = kt + \frac{1}{[A]_0}$
linear plot	[A} versus t	ln [A} versus t	$\frac{1}{[A]}$ versus t
slope	slope = – k	slope = – k	slope = k
half-life	$t_{\frac{1}{2}} = \frac{[A]_0}{2k}$	$t_{\frac{1}{2}} = \frac{0.693}{k}$	$t_{\frac{1}{2}} = \frac{1}{k\,[A]_0}$

You will be given a formula sheet, but a formula sheet is just a list of formulae. There is no explanation – you must recognize the different orders.

Special note: logarithms are a type of power (or exponential) calculation. Logarithms have a great deal of theoretical Math behind them, that you are not responsible for (take Math 1400 if you want to learn it).

Instead, learn to use logarithms on your scientific calculator. Be careful: there are two major types of logarithms – “log” common log and “ln” natural log (pronounced L – N). We will be using both in CHM 1200, but right now natural logs. Don’t mix them up! Scientific calculators usually have two buttons next to each other that look like this:



Notice the “shift” or “2nd” function above the “log” and “ln” buttons. They are called the “antilog” and “anti-ln” functions, meaning they reverse the log for algebra purposes. Beware: the anti-common log is not the same as scientific notation.

Logarithms have a special rounding rule – only the decimal places are significant figures.

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the Arrhenius Equation

The rate constant is not a true mathematical constant – it is not just a number, whose value never changes. The rate constant is a measurement.

The Arrhenius Equation for the rate constant shows important factors of a reaction, atom-by-atom, molecule-by-molecule, that would make it faster or slower:

$$k = A\ e^{-E_a/RT}$$

• A is the Arrhenius factor or frequency factor, which measures the frequency and efficiency of molecular collisions – if molecules never meet (never collide), they cannot react;

• E_a is the activation energy. Chemical bonds in the reactants must be broken, before new bonds can be formed to make products. I always say the activation energy measures the “kick” needed to get the reaction going. The higher the activation energy, the slower the reaction, and vice versa;

- T is the Kelvin temperature – the higher the temperature, the more collisions and the faster the reaction, and vice versa (this is one reason why we keep heating chemicals over a Bunsen burner in Lab – if the reaction is too slow at room temperature, maybe it'll be fast enough when blasted at 400 °C);

- R is the gas constant.

Be careful, since we are talking about energy (measured in Joules or kiloJoules), do NOT use $R = 0.0821\, L \cdot atm/mol \cdot K$, use $R = 8.314\ J/mol \cdot K$.

The basic Arrhenius Equation is inconvenient to use, and is often algebraically manipulated. For example, taking the natural log gives you:

$$\begin{array}{ccccc} \ln k = & -\frac{E_a}{R} & \frac{1}{T} & + & \ln A \\ y = & m & x & + & b \end{array}$$

Notice, you get a linear equation. This is very useful in Lab, where we graph data all the time.

In Lecture, this version is helpful to compare a reaction run at two different temperatures:

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Beware, since these are Math formulae, you must practice your Math skills.

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reaction mechanisms

A balanced equation, as introduced way back in Chapter 3, is not necessarily an accurate description of what actually happens during a chemical reaction, atom-by-atom, molecule-by-molecule.

Real chemical reactions often occur as a series of little reactions, one after another. Each little reaction is called an elementary step. The reaction mechanism is the whole series of elementary steps.

Note, although all reactions must have a mechanism describing what happens atom-by-atom, molecule-by-molecule, that does not mean figuring it out is easy (because atoms and molecules are so small), or even that we know what it is for many common reactions. However, chemical nanotechnology has gotten pretty good in the last 20-30 years, and many important mechanisms have been determined.

You are not responsible for memorizing any reaction mechanisms.

Instead, when examining a given reaction mechanism, recognize:

- the intermediates are a product of an earlier step in the mechanism that transfers to a later step as a reactant;
- the elementary steps must combine to the overall reaction;
- each elementary step is a balanced equation and has it own rate law, where the mole ratio coefficients are the rate orders;
- these individual rate laws must combine to the overall rate law;
- taking into account that rates of individual steps may be faster or slower than the other steps;
- and that the slowest step is the rate determining step – the entire reaction backs up behind the slowest step.

Catalysts were introduced in CHM 1100, when we said catalysts added to a reaction will make it faster, but will not be consumed by it. In CHM 1200, we add that catalysts change the reaction mechanism, where they will appear as a reactant of an earlier step in the mechanism and is recreated at a later step as a product, and they lower the overall activation energy to make the reaction faster.

Chapter 13: Kinetics Problems

Problem 1: In the reaction:

$$4\ \mathrm{PH_3}_{\,(g)} \longrightarrow \mathrm{P_4}_{\,(g)} + 6\ \mathrm{H_2}_{\,(g)}$$

an experiment is observed where PH_3 is consumed at 0.0048 mole per second in a 2.0-L container. What are the rates of production of P_4 and H_2 in this experiment?

Problem 2: The reaction:

$$2\ \mathrm{NO}_{(g)} + \mathrm{H_2}_{\,(g)} \longrightarrow \mathrm{N_2O}_{(g)} + \mathrm{H_2O}_{(g)}$$

is studied and the following rate data is measured:

trial	[NO] (mol/L)	$\left[H_2\right]$ mol/L	Initial Rate (M/s)
1	7.5×10^{-2}	2.2×10^{-3}	1.2×10^{-2}
2	1.5×10^{-3}	2.2×10^{-3}	3.0×10^{-3}
3	1.5×10^{-3}	6.6×10^{-3}	9.0×10^{-3}

Find the rate law and the value of the rate constant for the reaction.

Problem 3: Rate data is measured in four experiments for the reaction:

$$\mathrm{BrO_3^-}_{\,(aq)} + 5\ \mathrm{Br^-_{(aq)}} + 6\ \mathrm{H^+_{(aq)}} \longrightarrow 3\ \mathrm{Br_2}_{\,(l)} + 3\ \mathrm{H_2O}_{(l)}$$

trial	$\left[BrO_3^-\right]$ (mol/L)	$[Br^-]$ mol/L	$\left[H^+\right]$ mol/L	Initial Rate (M/s)
1	0.12	0.12	0.12	6.0×10^{-3}
2	0.24	0.12	0.12	1.2×10^{-2}
3	0.24	0.24	0.12	2.4×10^{-2}
4	0.12	0.12	0.24	2.4×10^{-2}

Using these data, determine the orders for all three reactants, the overall reaction order, and the value of the rate constant.

Problem 4: The dimerization of butadiene is:

$$2\ C_4H_{6\ (g)} \longrightarrow C_8H_{12\ (g)}$$

Concentration data for this reaction is collected at a particular temperature:

$[C_4H_6]$ **(mol/L)**	**time (s)**
0.1000	0
0.0625	90
0.0476	160
0.0370	250
0.0313	340
0.0270	415
0.0241	490
0.0208	585

(a) What is the reaction order? (b) What is the value of the rate constant for the reaction? (c) What would be the half-life for the dimerization of 0.0500 Molar butadiene?

Problem 5: The decomposition of gaseous dinitrogen pentoxide is a first-order reaction, with a half-life of 22 min at a certain temperature.

$$2\ N_2O_{5\ (g)} \longrightarrow 4\ NO_{2\ (g)} + O_{2\ (g)}$$

How much time is required for the concentration of N_2O_5 to decrease by 90%

Problem 6: The rate law for the decomposition of phosphine (PH_3) is:

$$rate = -\frac{\Delta\,[PH_3]}{\Delta t} = k\,[PH_3]$$

with a half-life of 75 s at a particular temperature. Calculate the concentration of 0.150 M PH_3 remaining after 12 minutes.

Problem 7: The decomposition of HI gas:

$$2\ \mathrm{HI}_{(g)} \longrightarrow \mathrm{H}_{2\ (g)} + \mathrm{I}_{2\ (g)}$$

has an activation energy of 186 kJ/mol. At 282 °C, the rate constant is 3.52×10^{-7} L/mol · s. What is the rate constant at 372 °C?

Problem 8: The gas-phase reaction between methane and diatomic sulfur is:

$$\mathrm{CH}_{4\ (g)} + 2\ \mathrm{S}_{2\ (g)} \longrightarrow \mathrm{CS}_{2\ (g)} + 2\ \mathrm{H_2S}_{(g)}$$

Experiments show that at 550 °C, the rate constant for this reaction is 1.1 L/mol · s, and at 625 °C, the rate constant is 6.4 L/mol · s. Calculate E_{a} for this reaction.

Problem 9: The rate constant for the decomposition of N_2O_5:

$$2\ \mathrm{N_2O}_{5\ (g)} \longrightarrow 4\ \mathrm{NO}_{2\,(g)} + \mathrm{O}_{2\ (g)}$$

is determined at various temperatures:

T (K)	**k (s^{-1})**
278	1.8×10^{-6}
298	3.5×10^{-5}
318	5.0×10^{-4}
338	4.9×10^{-3}
358	4.0×10^{-2}

Problem 10: The reaction: $2\ \mathrm{NO}_{(g)} + \mathrm{O}_{2\ (g)} \longrightarrow 2\ \mathrm{NO}_{2\ (g)}$

is known to have the rate law: $rate = k\,[\mathrm{NO}]^2\left[\mathrm{O_2}\right]$

Is this mechanism consistent with the rate law?

$$\begin{array}{lcr} \text{step 1} & \mathrm{NO} + \mathrm{O_2} \rightleftharpoons \mathrm{NO_2} + \mathrm{O} & \text{slow} \\ \text{step 2} & \mathrm{O} + \mathrm{NO} \longrightarrow \mathrm{NO_2} & \text{fast} \end{array}$$

Problem 11: For the reaction:

$$2\ H_{2\,(g)}\ + 2\ NO_{(g)}\ \longrightarrow\ N_{2\,(g)}\ +\ 2\ H_2O_{(g)}$$

a proposed mechanism for this reaction is

$$\begin{array}{lcr} \text{step 1} & 2\ NO\ \rightleftharpoons\ N_2O_2 & \text{fast, equilibrium} \\ \text{step 2} & N_2O_2\ +\ H_2\ \longrightarrow\ N_2O\ +\ H_2O & \text{slow} \\ \text{step 3} & N_2O\ +\ H_2\ \longrightarrow\ N_2\ +\ H_2O & \text{fast} \end{array}$$

What is the rate law derived from this mechanism?

Chapter 13: Kinetics Solutions

Solution 1: In the reaction:

$$4\ \mathrm{PH_3}_{\,(g)} \longrightarrow \mathrm{P_4}_{\,(g)} + 6\ \mathrm{H_2}_{\,(g)}$$

an experiment is observed where PH_3 is consumed at 0.0048 mole per second in a 2.0-L container. What are the rates of production of P_4 and H_2 in this experiment?

rate of PH_3 is:

$$rate\,(\mathrm{PH_3}) = \frac{\Delta\left[\mathrm{PH_3}\right]}{\Delta t} = \frac{-0.0048\ mol}{2.0\ L\cdot s} = \frac{-0.0024\ mol}{L\cdot s}$$

use rate expression:

$$rate = -\frac{1}{4}\frac{\Delta\left[\mathrm{PH_3}\right]}{\Delta t} = -\frac{\Delta\left[\mathrm{P_4}\right]}{\Delta t} = +\frac{1}{6}\frac{\Delta\left[\mathrm{H_2}\right]}{\Delta t}$$

$$\therefore\quad \frac{\Delta\left[\mathrm{P_4}\right]}{\Delta t} = \frac{1}{4}\frac{\Delta\left[\mathrm{PH_3}\right]}{\Delta t}$$

$$\frac{\Delta\left[\mathrm{P_4}\right]}{\Delta t} = \frac{1}{4}\frac{-0.0024\ mol}{L\cdot s}$$

$$\frac{\Delta\left[\mathrm{P_4}\right]}{\Delta t} = \frac{-0.0006\ mol}{L\cdot s}$$

$$\therefore\quad \frac{\Delta\left[\mathrm{H_2}\right]}{\Delta t} = -\frac{6}{4}\frac{\left[\mathrm{PH_3}\right]}{\Delta t}$$

$$\frac{\Delta\left[\mathrm{H_2}\right]}{\Delta t} = -\frac{3}{2}\frac{-0.0024\ mol}{L\cdot s}$$

$$\frac{\Delta\left[\mathrm{H_2}\right]}{\Delta t} = \frac{+0.0036\ mol}{L\cdot s}$$

or just use mole ratio:

$$\frac{-0.0024\ mol\ \mathrm{PH_3}}{L\cdot s} \times \frac{-1\ mol\ \mathrm{P_4}}{-4\ mol\ \mathrm{PH_3}} \approx \frac{-0.0006\ mol\ \mathrm{P_4}}{L\cdot s}$$

$$\frac{-0.0024\ mol\ \mathrm{PH_3}}{L\cdot s} \times \frac{+6\ mol\ \mathrm{H_2}}{-4\ mol\ \mathrm{PH_3}} \approx \frac{+0.0036\ mol\ \mathrm{H_2}}{L\cdot s}$$

Solution 2: The reaction:

$$2\ \mathrm{NO}_{(g)} \ + \ \mathrm{H}_{2\ (g)} \longrightarrow \ \mathrm{N_2O}_{(g)} \ + \ \mathrm{H_2O}_{(g)}$$

is studied and the following rate data is measured:

trial	**[NO] (mol/L)**	**$\left[\mathrm{H_2}\right]$ mol/L**	**Initial Rate (M/s)**
1	7.5×10^{-2}	2.2×10^{-3}	1.2×10^{-2}
2	1.5×10^{-3}	2.2×10^{-3}	3.0×10^{-3}
3	1.5×10^{-3}	6.6×10^{-3}	9.0×10^{-3}

Find the rate law and the value of the rate constant for the reaction.

The rate law must look like: $rate = k\,[\mathrm{NO}]^x \left[\mathrm{H_2}\right]^y$.

For each reactant, set up a ratio using two trials, where the concentrations of one reactant changes, but the other remains the same:

$$rate = k\,[\mathrm{NO}]^x \left[\mathrm{H_2}\right]^y$$

$$\frac{trial_1}{trial_2} = \frac{1.2 \times 10^{-2}}{3.0 \times 10^{-3}} = \left(\frac{7.5 \times 10^{-2}}{1.5 \times 10^{-3}}\right)^x \cancel{\left(\frac{2.2 \times 10^{-3}}{2.2 \times 10^{-3}}\right)^y}$$

$$4 = 2^x$$

$$\therefore \quad x = 2$$

The rate order of NO is 2.

$$rate = k\,[\mathrm{NO}]^x \left[\mathrm{H_2}\right]^y$$

$$\frac{trial_3}{trial_2} = \frac{9.0 \times 10^{-2}}{3.0 \times 10^{-3}} = \cancel{\left(\frac{1.5 \times 10^{-3}}{1.5 \times 10^{-3}}\right)^x} \left(\frac{6.6 \times 10^{-3}}{2.2 \times 10^{-3}}\right)^y$$

$$3 = 3^y$$

$$\therefore \quad y = 1$$

The rate order of $\mathrm{H_2}$ is 1.

The rate law is: $rate = k\,[\mathrm{NO}]^2 \left[\mathrm{H_2}\right]$

Use the rate law just found to find rate constant:

$$rate = k\,[NO]^2\,[H_2]$$

$$\therefore \quad k = \frac{rate}{[NO]^2\,[H_2]}$$

$$trial_1 = k = \frac{1.2\times10^{-2}}{\left(7.5\times10^{-2}\right)^2\,2.2\times10^{-3}}$$

$$k \approx 9.7\times10^{2}$$

Solution 3: Rate data is measured in four experiments for the reaction:

$$BrO_3^-{}_{(aq)} + 5\ Br^-_{(aq)} + 6\ H^+_{(aq)} \longrightarrow 3\ Br_{2\,(l)} + 3\ H_2O_{(l)}$$

trial	**$[BrO_3^-]$ (mol/L)**	**$[Br^-]$ mol/L**	**$[H^+]$ mol/L**	**Initial Rate (M/s)**
1	0.12	0.12	0.12	6.0×10^{-3}
2	0.24	0.12	0.12	1.2×10^{-2}
3	0.24	0.24	0.12	2.4×10^{-2}
4	0.12	0.12	0.24	2.4×10^{-2}

Using these data, determine the orders for all three reactants, the overall reaction order, and the value of the rate constant.

The rate law must look like: $rate = k\,[BrO_3^-]^x\,[Br^-]^y\,[H^+]^z$.

Three reactants needs three ratios:

$$rate = \cancel{k}\,[BrO_3^-]^x\,[Br^-]^y\,[H^+]^z$$

$$\frac{trial_2}{trial_1} = \frac{1.2\times10^{-2}}{6.0\times10^{-3}} = \left(\frac{0.24}{0.12}\right)^x \cancel{\left(\frac{0.12}{0.12}\right)^y}\,\cancel{\left(\frac{0.12}{0.12}\right)^z}$$

$$2 = 2^x$$

$$\therefore \quad x = 1$$

Rate order of BrO_3^- is 1.

$$
\begin{aligned}
rate &= \cancel{k}\left[\mathrm{BrO_3^-}\right]^x \left[\mathrm{Br^-}\right]^y \left[\mathrm{H^+}\right]^z \\
\frac{trial_3}{trial_2} = \frac{2.4\times10^{-2}}{1.2\times10^{-2}} &= \cancel{\left(\frac{0.12}{0.12}\right)^x} \left(\frac{0.24}{0.12}\right)^y \cancel{\left(\frac{0.12}{0.12}\right)^z} \\
2 &= 2^y \\
\therefore \quad y &= \color{red}{1}
\end{aligned}
$$

Rate order of $\mathrm{Br^-}$ is 1.

$$
\begin{aligned}
rate &= \cancel{k}\left[\mathrm{BrO_3^-}\right]^x \left[\mathrm{Br^-}\right]^y \left[\mathrm{H^+}\right]^z \\
\frac{trial_4}{trial_1} = \frac{2.4\times10^{-2}}{6.0\times10^{-3}} &= \cancel{\left(\frac{0.12}{0.12}\right)^x} \cancel{\left(\frac{0.12}{0.12}\right)^y} \left(\frac{0.24}{0.12}\right)^z \\
4 &= 2^z \\
\therefore \quad z &= \color{red}{2}
\end{aligned}
$$

Rate order of $\mathrm{H^+}$ is 2.

The overall reaction order is $1 + 1 + 2 = \color{red}{4}$.

With the rate law as: $rate = k\left[\mathrm{BrO_3^-}\right]\left[\mathrm{Br^-}\right]\left[\mathrm{H^+}\right]^2$

To find rate constant:

$$
\begin{aligned}
rate &= k\left[\mathrm{BrO_3^-}\right]\left[\mathrm{Br^-}\right]\left[\mathrm{H^+}\right]^2 \\
\therefore \quad k &= \frac{rate}{\left[\mathrm{BrO_3^-}\right]\left[\mathrm{Br^-}\right]\left[\mathrm{H^+}\right]^2} \\
trial_1 = k &= \frac{6.0\times10^{-3}}{(0.12)(0.12)(0.12)^2} \\
k &\approx \color{red}{29}
\end{aligned}
$$

Solution 4: The dimerization of butadiene is:

$$2\ \mathrm{C_4H_6}_{\,(g)} \longrightarrow \mathrm{C_8H_{12}}_{\,(g)}$$

Concentration data for this reaction is collected at a particular temperature:

$\left[\mathrm{C_4H_6}\right]$ **(mol/L)**	**time (s)**
0.1000	0

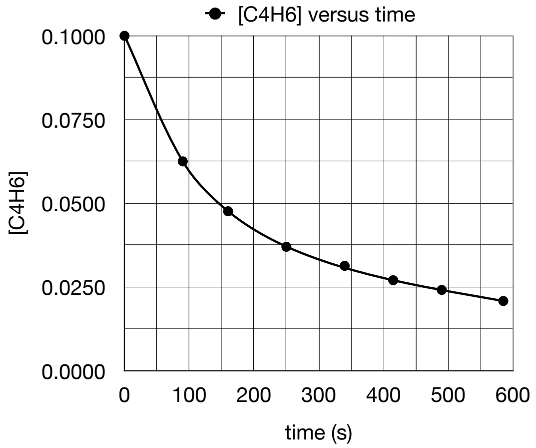
$[C_4H_6]$ (mol/L)	time (s)
0.0625	90
0.0476	160
0.0370	250
0.0313	340
0.0270	415
0.0241	490
0.0208	585

(a) What is the reaction order? (b) What is the value of the rate constant for the reaction? (c) What would be the half-life for the dimerization of 0.0500 Molar butadiene?

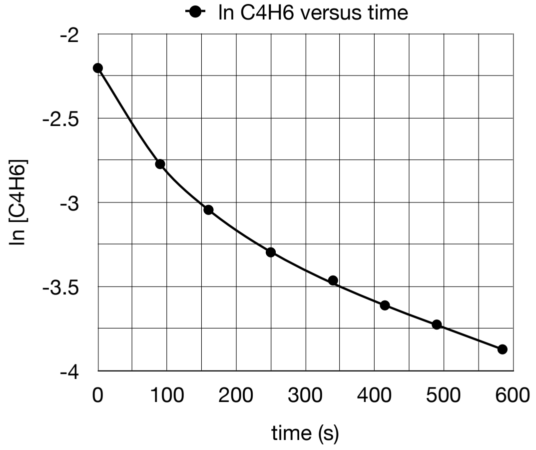
(a) For a zeroth-order reaction, the graph of the $[C_4H_6]$ (y-axis) versus time (x-axis) will give a linear function (straight line). For a first-order reaction, the graph of the NATURAL LOG of $[C_4H_6]$ (y-axis) versus time will be a straight line. And, for a second-order reaction, the graph of the INVERSE of $[C_4H_6]$ (y-axis) versus time will be linear.

So first, compute natural log and inverse of all $[C_4H_6]$ values:

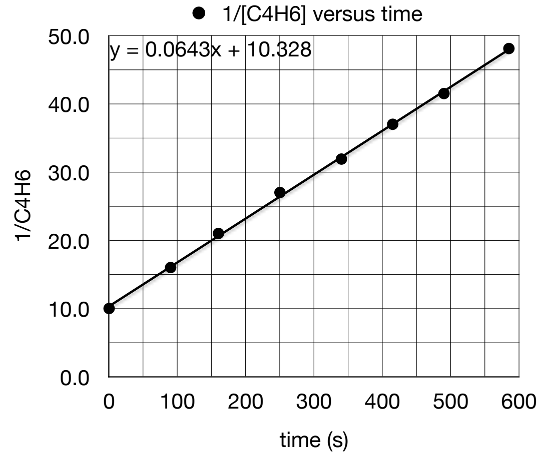
$[C_4H_6]$ (mol/L)	time (s)	ln $[C_4H_6]$	$\frac{1}{[C_4H_6]}$
0.1000	0	–2.203	10.0
0.0625	90	–2.773	16.0
0.0476	160	–3.045	21.0
0.0370	250	–3.297	27.0
0.0313	340	–3.464	31.9
0.0270	415	–3.612	37.0
0.0241	490	–3.726	41.5
0.0208	585	–3.873	48.1



The slope of the $[C_4H_6]$ versus time graph is not linear. The reaction is NOT zeroth-order.



The slope of the natural log of $[C_4H_6]$ versus time graph is not linear. The reaction is NOT first-order.



The slope of the inverse of $[C_4H_6]$ versus time graph is linear. The reaction is SECOND-ORDER.

Remember, these graphs do not have to be perfect. They only need to be good enough for you to see which one is linear.

(b) The slope of second-order line is the second-order rate constant. The approximate slope of the graph of a straight line of real data can most simply be found using the two extreme data points. (Remember, this is not proper in Math class. You're supposed to use two non-data points, determined from the line you just constructed, to find the slope.)

$$\begin{aligned} slope = m &= \frac{\Delta y}{\Delta x} \\ &= \frac{y_2 - y_1}{x_2 - x_1} \\ &= \frac{48.1 - 10.1}{585 - 0} \\ &= \frac{38.1}{585} \\ m \equiv k &\approx 6.5 \times 10^{-2} \end{aligned}$$

(c) The half-life of a second-order reaction is given by the formula:

$$t_{\frac{1}{2}} = \frac{1}{k\left[\mathrm{C_4H_6}\right]_0}$$

$$t_{\frac{1}{2}} = \frac{1}{6.5 \times 10^{-2}\left[0.0500\right]}$$

$$t_{\frac{1}{2}} \approx 3.1 \times 10^{2}\ s$$

Notice: the actual chemical reaction is not used, only the data collected about the reaction.

Solution 5: The decomposition of gaseous dinitrogen pentoxide is a first-order reaction, with a half-life of 22 min at a certain temperature.

$$2\ \mathrm{N_2O_5}_{\,(g)} \longrightarrow 4\ \mathrm{NO_2}_{\,(g)} + \mathrm{O_2}_{\,(g)}$$

How much time is required for the concentration of N_2O_5 to decrease by 90%

Use the first-order half-life formula and time equation:

$$\begin{aligned} t_{\frac{1}{2}} &= \frac{0.693}{k} \\ \therefore \quad k &= \frac{0.693}{t_{\frac{1}{2}}} \\ k &= \frac{0.693}{22\ min} \\ k &= 3.15 \times 10^{-2}\ min^{-1} \end{aligned}$$

$$\begin{aligned} \ln\left[A\right]_f &= -kt + \ln\left[A\right]_0 \\ \ln\left[\mathrm{N_2O_5}\right]_f &= -kt + \ln\left[\mathrm{N_2O_5}\right]_0 \\ \ln\left[10\,\%\right] &= -3.15 \times 10^{-2}\ t + \ln\left[100\,\%\right] \\ 2.303 &\approx -3.15 \times 10^{-2}\ t + 4.605 \\ -2.302 &\approx -3.15 \times 10^{-2}\ t \\ \therefore \quad t &\approx 73\ min \end{aligned}$$

Notice: half-lives problems are more Math than Chemistry, because they have specific formulae.

Solution 6: The rate law for the decomposition of phosphine (PH_3) is:

$$rate = -\frac{\Delta\left[\mathrm{PH_3}\right]}{\Delta t} = k\left[\mathrm{PH_3}\right]$$

with a half-life of 75 s at a particular temperature. Calculate the concentration of 0.150 M PH_3 remaining after 12 minutes.

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$\therefore \quad k = \frac{0.693}{t_{\frac{1}{2}}}$$

$$k = \frac{0.693}{75\ s}$$

$$k = 9.24 \times 10^{-3}\ s^{-1}$$

$$\ln\left[A\right]_f = -kt + \ln\left[A\right]_0$$

$$\ln\left[\mathrm{PH_3}\right]_f = -kt + \ln\left[\mathrm{PH_3}\right]_0$$

$$\ln\left[\mathrm{PH_3}\right]_f = -9.24 \times 10^{-3}\ (720) + \ln\left[0.150\right]$$

$$\ln\left[\mathrm{PH_3}\right]_f \approx -6.653 + (-1.897)$$

$$\ln\left[\mathrm{PH_3}\right]_f \approx -8.550$$

$$e^{\ln\left[\mathrm{PH_3}\right]_f} \approx e^{-8.550}$$

$$\therefore \quad \left[\mathrm{PH_3}\right]_f \approx 1.94 \times 10^{-4}\ M$$

Solution 7: The decomposition of HI gas:

$$2\ \mathrm{HI}_{(g)} \longrightarrow \mathrm{H}_{2\ (g)} + \mathrm{I}_{2\ (g)}$$

has an activation energy of 186 kJ/mol. At 282 °C, the rate constant is 3.52×10^{-7} L/mol · s. What is the rate constant at 372 °C?

Remember your units:

$$E_a = 182\ kJ/mol \times \frac{1000\ J}{kJ} = 182{,}000\ J$$

$$T_1 = 282^{\circ}C + 273 = 555\ K$$

$$k_1 = 3.52 \times 10^{-7}\ L/mol \cdot s$$

$$T_2 = 372^{\circ}C + 273 = 645\ K$$

$$R = 8.314\ J/mol \cdot K$$

unknown: $k_2 = ?$

Since this problem is comparing two temperatures, use the two-temperature version of the Arrhenius Equation:

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\ln\left(\frac{k_2}{3.52\times10^{-7}}\right) = -\frac{182{,}000}{8.314}\left(\frac{1}{645}-\frac{1}{555}\right)$$

$$\ln\left(\frac{k_2}{3.52\times10^{-7}}\right) \approx -21{,}891\left(0.001550-0.001802\right)$$

$$\ln\left(\frac{k_2}{3.52\times10^{-7}}\right) \approx -21{,}891\left(-0.000251\right)$$

$$\ln\left(\frac{k_2}{3.52\times10^{-7}}\right) \approx 5.504$$

$$e^{\ln\left(\frac{k_2}{3.52\times10^{-7}}\right)} \approx e^{5.504}$$

$$\frac{k_2}{3.52\times10^{-7}} \approx 246$$

$$k_2 \approx 8.65\times10^{-5}\ L/mol\cdot s$$

Be aware: there are other ways to do the algebra, but you should finish with the same answer.

Solution 8: The gas-phase reaction between methane and diatomic sulfur is:

$$CH_{4\,(g)} + 2\ S_{2\,(g)} \longrightarrow CS_{2\,(g)} + 2\ H_2S_{(g)}$$

Experiments show that at 550 °C, the rate constant for this reaction is 1.1 L/mol · s, and at 625 °C, the rate constant is 6.4 L/mol · s. Calculate E_a for this reaction.

pay attention to the correct units:

$T_1 = 550^{\circ}C + 273 = 823\ K$

$k_1 = 1.1\ L/mol\cdot s$

$T_2 = 625^{\circ}C + 273 = 898\ K$

$k_2 = 6.4\ L/mol\cdot s$

$R = 8.314\ J/mol\cdot K$

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\ln\left(\frac{6.4}{1.1}\right) = -\frac{E_a}{8.314}\left(\frac{1}{898}-\frac{1}{823}\right)$$

$$\ln\left(5.818\right) \approx -\frac{E_a}{8.314}\left(0.001114-0.001215\right)$$

$$1.761 \approx -\frac{E_a}{8.314}(-0.000101)$$

$$1.761 \approx E_a\left(1.22\times 10^{-5}\right)$$

$$\therefore \quad E_a \approx 1.44\times 10^{5}\ J/mol$$

$$E_a \approx 144\ kJ/mol$$

Solution 9: The rate constant for the decomposition of N_2O_5:

$$2\ N_2O_{5\,(g)} \longrightarrow 4\ NO_{2\,(g)} + O_{2\,(g)}$$

is determined at various temperatures:

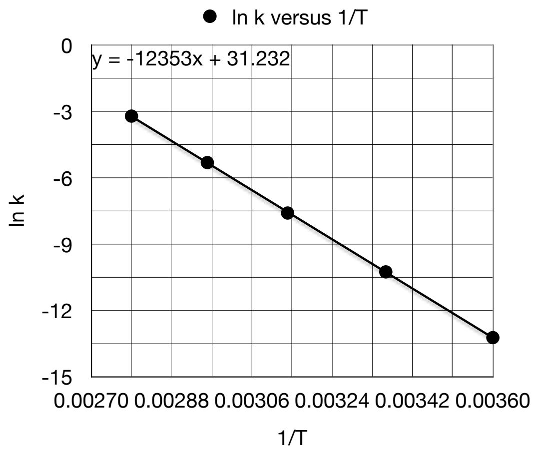
T (K)	**k (s^{-1})**
278	1.8×10^{-6}
298	3.5×10^{-5}
318	5.0×10^{-4}
338	4.9×10^{-3}
358	4.0×10^{-2}

According to the Arrhenius Equation, the graph of the natural log of k (y-axis) versus the inverse of Kelvin temperature (x-axis) is linear (a straight line).

$$\begin{aligned}\ln k &= -\frac{E_a}{R}\frac{1}{T} + \ln A\\ y &= \quad m \ \ x \ + \ b\end{aligned}$$

The slope of this line gives the activation energy.

T (K)	**k (s^{-1})**	**1/T**	**ln k**
278	1.8×10^{-6}	0.00360	–13.23
298	3.5×10^{-5}	0.00336	–10.26
318	5.0×10^{-4}	0.00314	–7.60
338	4.9×10^{-3}	0.00296	–5.32
358	4.0×10^{-2}	0.00279	–3.22



Since the graph is known to be linear, you don't really need to plot it, except as a check. Just skip to the slope.

The approximate slope of the graph of a straight line of experimental data can be found most simply by using the two extreme data points.

Finish by using the slope to find activation energy.

$$\begin{aligned} slope = m &= \frac{\Delta y}{\Delta x} \\ &= \frac{y_2 - y_1}{x_2 - x_1} \\ &= \frac{-3.22 - (-13.23)}{0.00279 - 0.00360} \\ &= \frac{10.01}{-0.00081} \\ m &\approx -1.24 \times 10^4 \end{aligned}$$

$$\begin{aligned} m &= -\frac{E_a}{R} \\ \therefore \quad E_a &= -mR \\ &= -\left(-1.24 \times 10^4\right)(8.314) \\ E_a &\approx 1.03 \times 10^5 \ J/mol \\ E_a &\approx 1.0 \times 10^2 \ kJ/mol \end{aligned}$$

Solution 10: The reaction: $2\ NO_{(g)} + O_{2\ (g)} \longrightarrow 2\ NO_{2\ (g)}$

is known to have the rate law: $rate = k\,[NO]^2\,[O_2]$

Is this mechanism consistent with the rate law?

step 1	$NO + O_2 \rightleftharpoons NO_2 + O$	slow
step 2	$O + NO \longrightarrow NO_2$	fast

Since step 1 is the slow step, it is the rate determining step. Ignore step 2. The rate law of step 1 is the overall rate law. Remember, the coefficients of an elementary step are the orders for its rate law.

$$rate = k\,[\mathrm{NO}]\,[\mathrm{O_2}]$$

This does NOT match the known rate law. Therefore the mechanism cannot be correct.

Solution 11: For the reaction:

$$2\ \mathrm{H_2}_{\,(g)} + 2\ \mathrm{NO}_{(g)} \longrightarrow \mathrm{N_2}_{\,(g)} + 2\ \mathrm{H_2O}_{(g)}$$

a proposed mechanism for this reaction is

$$\begin{array}{lcr} \text{step 1} & 2\ \mathrm{NO} \rightleftharpoons \mathrm{N_2O_2} & \text{fast, equilibrium} \\ \text{step 2} & \mathrm{N_2O_2} + \mathrm{H_2} \longrightarrow \mathrm{N_2O} + \mathrm{H_2O} & \text{slow} \\ \text{step 3} & \mathrm{N_2O} + \mathrm{H_2} \longrightarrow \mathrm{N_2} + \mathrm{H_2O} & \text{fast} \end{array}$$

What is the rate law derived from this mechanism?

Since step 2 is the slow step, it is the rate determining step. Ignore step 3. The procedure is to set up the rate laws of steps 1 and 2, and then combine them Mathematically, (as simultaneous equations) through the intermediate. Remember, the coefficients of an elementary step are the orders for its rate law.

$$rate_1 = k_{forward}\,[\mathrm{NO}]^2 = k_{reverse}\,[\mathrm{N_2O_2}]$$

$$\therefore \quad [\mathrm{N_2O_2}] = \frac{k_{forward}\,[\mathrm{NO}]^2}{k_{reverse}}$$

$$\begin{aligned} rate_2 &= k_2\,[\mathrm{N_2O_2}]\,[\mathrm{H_2}] \\ &= k_2\,\frac{k_{forward}\,[\mathrm{NO}]^2}{k_{reverse}}\,[\mathrm{H_2}] \\ &= \frac{k_2\ k_{forward}}{k_{reverse}}\,[\mathrm{NO}]^2\,[\mathrm{H_2}] \\ rate &= k\,[\mathrm{NO}]^2\,[\mathrm{H_2}] \end{aligned}$$

Sometimes you can just add steps 1 and 2 into a new equation, and use its coefficients for the overall rate law:

$$\begin{array}{lc} \text{step 1} & 2\ \mathrm{NO} \rightleftharpoons \cancel{\mathrm{N_2O_2}} \\ \text{step 2} & \cancel{\mathrm{N_2O_2}} + \mathrm{H_2} \longrightarrow \mathrm{N_2O} + \mathrm{H_2O} \\ \text{step 1+2} & 2\ \mathrm{NO} + \mathrm{H_2} \longrightarrow \mathrm{N_2O} + \mathrm{H_2O} \end{array}$$

$$rate = k\,[\mathrm{NO}]^2\,[\mathrm{H_2}]$$

Chapter 20: Nuclear reactions

RECALL from Chapter 2: The smallest possible particle of an element is an atom. The Periodic Table lists of all the elements. Atoms are made of even smaller subatomic particles: protons, neutrons and electrons. Atoms have a structure: protons and neutrons packed into a ball at the center of the atom called the nucleus, with electrons outside the nucleus, orbiting at different distances in energy shells. Atomic number, Z, is the number of protons. Mass number, A, is the sum of protons plus neutrons.

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natural nuclear reactions

Remember: a reaction is a change. Nuclear means the protons or neutrons in the nucleus of an atom changes. And natural means these changes occur all around us in nature (although they are rare).

Some atoms are RADIOACTIVE (they give off RADIATION), because their nuclei are UNSTABLE. If you try to build atoms with random numbers of protons, neutrons and electrons, you will find that most will fall apart.

A GRAPH of all nuclei, comparing the number of neutrons versus the number of protons, will show that stable atoms form a narrow diagonal strip curving up the middle. This is called the BAND OF STABILITY. Any nucleus that is not on the band of stability is radioactive. They will DECAY or TRANSMUTE – change into a different nuclei closer to or on the band of stability.

- When describing a nuclear reaction, we write a NUCLEAR EQUATION:
- A nuclear equation is read from left to right.
- The atomic symbols on the left side of the equation represent the PARENT nuclei; they are the nuclei the reaction begins with (reactants). If there is more than one reactant, they are separated by PLUS (+) signs.
- The atomic symbols on the right side of the equation represent the DAUGHTER nuclei products; they are the nuclei the reaction ends with (products). If there is more than one product, they are separated by PLUS (+) signs.
- The reactants and products are separated by a right pointing ARROW. The arrow indicates that the reactants change into products.

- All atomic symbols should include the atomic number and mass number. The atomic number is sometimes omitted (because you can look it up on the Periodic Table), but the mass number must be given (because that's not on the Periodic Table).

- The COEFFICIENT (whole number) to the immediate left of each atomic symbol counts the atoms. If there is no number written, it is one (1).

- Nuclear reactions are NOT the same as chemical reactions. Atoms do not change in chemical reactions, but they are supposed to change in nuclear reactions.

There are three major types of radioactivity – alpha (**α**), beta (**β**) and gamma (**γ**) depending on why the atom is unstable.

α, **β** and **γ** are the first three letters of the Greek alphabet. When radioactivity was first discovered, scientists had no idea what was going on – except that there were three different things going on. So they were just called a, b and c (well g) in Greek. We now know that an alpha particle is a group of two (2) protons and two (2) neutrons (a helium nucleus), a beta particle is an electron and a gamma ray is a high energy PHOTON – a high energy particle (quantum) of LIGHT.

- ALPHA DECAY (**α**) occurs if the nucleus is too large (is beyond the end of the band of stability). Bismuth (atomic number 83) is the largest stable atom. Polonium and larger atoms (atomic number 84 and higher) are all unstable simply because they have too many protons and neutrons. The unstable nucleus spits out (2) protons and (2) neutrons to become smaller – I like to call it the "alpha diet." The atomic number decreases by two (2) and the mass number decreases by four (4).

Note: alpha particles have heavy mass, positive charge and have least penetrating power, compared to the others. (Penetrating power is a measure of "dangerous-ness." All nuclear radiation is dangerous, if you don't know what you're doing, but alpha is "least" dangerous. Don't play around with the samples in the Nuclear Reactions Lab.)

- BETA DECAY (**β**) occurs if the nucleus has too many neutrons (the ratio of neutrons to protons is too high and the nucleus is above the band of stability). To eliminate a neutron in the unstable nucleus, one of them changes into a proton and an electron. The protons belongs in the nucleus, but the electron is spit out as the beta particle. The atomic number increases by one (1), while the mass number remains the same.

Note: beta particles have light mass, negative charge and are more penetrating than alpha.

- GAMMA DECAY (**γ**) occurs if the nucleus is in an excited state – has extra energy. Just like an excited electron in the electron shells will transition back to ground state, and release a photon, an excited nucleus will transition back to ground state too, releasing the extra energy as a photon (light). The difference is that gamma photons have much higher energy compared to visible light photons. This is called isomeric transition to ground state. Both the atomic number and the mass number remain the same.

Note: Gamma rays have no mass, no charge and are most penetrating. (Since gamma has most penetrating power, it is the most dangerous. If you overdose on gamma rays, you won't become the Hulk; you'll probably die. Luckily, gamma is very rare.)

Note: Pure gamma radiation (as metastable isomeric transition) is extremely rare, but often follows alpha or beta radiation, as the disturbed nucleus makes an immediate shift to ground state.

You do not need to memorize any specific atoms as decaying by alpha, beta or gamma, but if you are told how the atom will decay, you must be able to write the reaction.

Memorize these special atomic symbols, needed to write common nuclear reactions:

particle	symbol	equivalent	notes
alpha	**α**	${}^{4}_{2}\alpha = {}^{4}_{2}\mathrm{He}$	two protons + two neutrons = He nucleus
beta	**β**	${}^{0}_{-1}\beta = {}^{0}_{-1}e$	beta = electron
gamma	**γ**	${}^{0}_{0}\gamma$	very high energy photon; a quantum of light
proton	p^+	${}^{1}_{1}p = {}^{1}_{1}\mathrm{H}$	proton = H nucleus
neutron	n^0	${}^{1}_{0}n$	
electron	e^-	${}^{0}_{-1}e$	
positron	e^+	${}^{0}_{+1}\beta$	positive electron is antimatter

Note: A positron is a particle of ANTIMATTER. Antimatter is identical to normal matter, except that it is opposite in some way. Positron is short for positive electron. A positron is identical to an electron, except it has a positive charge. Antimatter is extremely rare, but does show up in some nuclear reactions. If you do not continue with nuclear science, you will probably never run into antimatter again, There are other types of natural nuclear reactions, but these are much rarer than the others: positron emission (also called beta-plus decay), electron capture (also called K-capture) and spontaneous fission.

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artificial nuclear reactions

There are all sorts of artificial nuclear reactions – nuclear reactions that only occur on the Earth through human manipulation. The two most important types are NUCLEAR FISSION and NUCLEAR FUSION.

Fission means splitting a large nucleus into smaller ones by hitting it with a neutron.

In a fission reaction, the reactant nucleus will produce unpredictable product nuclei, but it will be around a sixty/forty split.

Fission products include some neutrons as debris. If controlled properly, they can be focused to cause other fissions with more neutrons, which can do more fissions, and so on. This is called a CHAIN REACTION.

Fission reactions also produce highly radioactive products – called NUCLEAR WASTE, which are extremely difficult to dispose of.

Fusion means squeezing small nuclei into a larger one under extremely high pressure and temperature.

Fission and fusion reactions can be very dangerous because they can release enormous amounts of energy. Most nuclear reactions, of any type, are about one million times more powerful than chemical reactions.

A nuclear power plant uses the energy released by the fission reaction of uranium-235 to produce electricity. There are about 100 nuclear power plant in the United States, producing about 20% of the country's electricity since about 1975. The closest is the Indian Point plant, about 60 miles north of Kingsborough.

Stars, including the Sun, naturally produce their light by nuclear fusion reactions.

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half-lives

Like any other reaction, time kinetics is important for nuclear reactions.

Since all radioactivity is first-order, the radioactivity time equation is the same as the first-order time equation from Chapter 12:

$$\ln \left[A\right]_f = -kt + \ln \left[A\right]_0$$

although some people write “N” instead of “A” and combine like terms.

$$\ln\left(\frac{N_f}{N_0}\right) = -kt$$

the half-life formula is also the same:

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

Note: unlike chemical reactions, the kinetics of nuclear reactions cannot be altered by changing temperature.

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mass defect and binding energy

If you very carefully weigh the reactants and products of a nuclear reaction, you will discover that they are very slightly different.

For example, the mass of an atomic nucleus is very slightly less than the mass of the separate component protons and neutrons. This is called the mass defect, **Δ**m – “defect” because conservation of matter says that that total mass does not change – matter can only be changed from one form to another.

Therefore, the mass loss cannot just go “poof” and disappear into nothingness,.

According to the Einstein equation of mass-energy equivalence:

$$E = mc^2$$

(m is mass, E is energy, c is the constant speed of light – $c \approx 2.998 \times 10^8\ m/s$)

the mass is converted into the energy that “glues” the nucleus together – the binding energy. (Yes, this is THE Albert Einstein. Impress your friends.)

Remember this conversion factor:

$$1\ g = 6.022 \times 10^{23}\ amu \ \text{(Avogadro's Number)}$$

Einstein was a Physicist, not a Chemist, so also remember, the mass must be in kilograms, and the energy will be in Joules.

Chapter 20: Nuclear reactions Problems

Problem 1: Write the balanced nuclear equations when:

(a) uranium-238 decays by alpha:

(b) carbon-14 emits beta particles:

(c) nickel-60 emits gamma rays:

Problem 2: Fill in the blanks to balance the following nuclear equations:

(a) $^{90}\text{Sr} \longrightarrow {}^{90}\text{Y} + \_$

(b) $^{226}\text{Ra} \longrightarrow {}^{222}\text{Rn} + \_$

(c) $^{27}\text{Al} + \alpha \longrightarrow {}^{30}\text{P} + \_$

(d) $^{55}\text{Co} \longrightarrow {}^{55}\text{Fe} + \_$

(e) $^{195}\text{Au} + \_ \longrightarrow {}^{195}\text{Pt}$

(f) $^{234m}\text{Pa} \longrightarrow {}^{234}\text{Pa} + \_$

(g) $\_ \longrightarrow \beta^- + {}^{131}\text{Xe}$

(h) $\_ \longrightarrow \alpha + {}^{230}\text{Ra}$

(i) $^{14}\text{N} + {}^{4}\text{He} \longrightarrow {}^{17}\text{O} + \_$

(j) $^{249}\text{Cf} + {}^{12}\text{C} \longrightarrow \_ + 4\ \text{n}^0$

Problem 3: Phosphorus-32 has a half-life of 14.3 days. What percentage of a ^{32}P sample would remain after 7.0 weeks?

Problem 4: A wood sample found in an archeological dig is measured to have a carbon-14 decay count of 7.82 counts per minute per gram of carbon. The carbon-14 count from a living tree is 13.6 counts per minute per gram of carbon. How old is the sample? The half-life of carbon-14 is 5730 years.

Problem 5: The mass of an oxygen-16 nucleus is 15.990881 amu. What is the binding energy per nucleon, in kJ/nucleon, and per mole of nuclei, in kJ/mol? (The mass of a proton is 1.007276 amu, and the mass of a neutron is 1.008665 amu.)

Chapter 20: Nuclear reactions Solutions

Solution 1: Write the balanced nuclear equations when:

(a) uranium-238 decays by alpha:

$$ {}^{238}_{92}\mathrm{U} \longrightarrow {}^{4}_{2}\alpha + {}^{234}_{90}\mathrm{Th} \quad \text{or} \quad {}^{238}_{92}\mathrm{U} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{234}_{90}\mathrm{Th} $$

(b) carbon-14 emits beta particles:

$$ {}^{14}_{6}\mathrm{C} \longrightarrow {}^{0}_{-1}\beta + {}^{14}_{7}\mathrm{N} \quad \text{or} \quad {}^{14}_{6}\mathrm{C} \longrightarrow {}^{0}_{-1}e + {}^{14}_{7}\mathrm{N} $$

(c) nickel-60 emits gamma rays:

$$ {}^{60}_{28}\mathrm{Ni} \longrightarrow {}^{0}_{0}\gamma + {}^{60}_{28}\mathrm{Ni} $$

Solution 2: Fill in the blanks to balance the following nuclear equations:

(a) ${}^{90}_{38}\mathrm{Sr} \longrightarrow {}^{90}_{39}\mathrm{Y} + \underline{{}^{0}_{-1}\beta}$ or ${}^{90}_{38}\mathrm{Sr} \longrightarrow {}^{90}_{39}\mathrm{Y} + \underline{{}^{0}_{-1}e}$

(b) ${}^{226}_{88}\mathrm{Ra} \longrightarrow {}^{222}_{86}\mathrm{Rn} + \underline{{}^{4}_{2}\alpha}$ or ${}^{226}_{88}\mathrm{Ra} \longrightarrow {}^{222}_{86}\mathrm{Rn} + \underline{{}^{4}_{2}\mathrm{He}}$

(c) ${}^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{30}_{15}\mathrm{P} + \underline{{}^{1}_{0}\mathrm{n}}$

(d) ${}^{55}_{27}\mathrm{Co} \longrightarrow {}^{55}_{26}\mathrm{Fe} + \underline{{}^{0}_{+1}\beta}$

(e) ${}^{195}_{79}\mathrm{Au} + \underline{{}^{0}_{-1}\beta} \longrightarrow {}^{195}_{78}\mathrm{Pt}$ or ${}^{195}_{79}\mathrm{Au} + \underline{{}^{0}_{-1}e} \longrightarrow {}^{195}_{78}\mathrm{Pt}$

(f) ${}^{234m}_{91}\mathrm{Pa} \longrightarrow {}^{234}_{91}\mathrm{Pa} + \underline{{}^{0}_{0}\gamma}$

(g) $\underline{{}^{131}_{53}\mathrm{I}} \longrightarrow {}^{0}_{-1}\beta + {}^{131}_{54}\mathrm{Xe}$

(h) $\underline{{}^{234}_{90}\mathrm{Th}} \longrightarrow {}^{4}_{2}\alpha + {}^{230}_{88}\mathrm{Ra}$

(i) $^{14}_{7}\mathrm{N} + ^{4}_{2}\mathrm{He} \longrightarrow ^{17}_{8}\mathrm{O} + \underline{^{1}_{1}\mathrm{H}}$ or $^{14}_{7}\mathrm{N} + ^{4}_{2}\mathrm{He} \longrightarrow ^{17}_{8}\mathrm{O} + \underline{^{1}_{1}\mathrm{p}}$

(j) $^{249}_{98}\mathrm{Cf} + ^{12}_{6}\mathrm{C} \longrightarrow \underline{^{257}_{104}\mathrm{Rf}} + 4\,^{1}_{0}\mathrm{n}$

Solution 3: Phosphorus-32 has a half-life of 14.3 days. What percentage of a ^{32}P sample would remain after 7.0 weeks?

$$7.0\ weeks \times \frac{7\ days}{1\ week} = 49\ days$$

It does not matter what the reaction is. All radioactivity, **α**, **β** and **γ**, is first-order.

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$
$$\therefore \quad k = \frac{0.693}{t_{\frac{1}{2}}}$$
$$= \frac{0.693}{14.3\ days}$$
$$k \approx 0.04846\ days^{-1}$$

$$\ln\left[A\right]_f = -kt + \ln\left[A\right]_0$$
$$\ln\left[^{32}\mathrm{P}\right]_f = -kt + \ln\left[^{32}\mathrm{P}\right]_0$$
$$\ln\left[^{32}\mathrm{P}\right]_f \approx -0.04846\,(49) + \ln\left[100\,\%\right]$$
$$\ln\left[^{32}\mathrm{P}\right]_f \approx -2.375 + 4.605$$
$$\ln\left[^{32}\mathrm{P}\right]_f \approx 2.230$$
$$e^{\ln\left[^{32}\mathrm{P}\right]_f} \approx e^{2.230}$$
$$\therefore \quad \left[^{32}\mathrm{P}\right]_f \approx 9.3\,\%$$

Solution 4: A wood sample found in an archeological dig is measured to have a carbon-14 decay count of 7.82 counts per minute per gram of carbon. The carbon-14 count from a living tree is 13.6 counts per minute per gram of carbon. How old is the sample? The half-life of carbon-14 is 5730 years.

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$
$$\therefore \quad k = \frac{0.693}{t_{\frac{1}{2}}}$$
$$= \frac{0.693}{5730\ years}$$
$$k \approx 1.21 \times 10^{-4}\ years^{-1}$$

$$\ln\left[A\right]_f = -kt + \ln\left[A\right]_0$$
$$\ln\left[^{14}\mathrm{C}\right]_f = -kt + \ln\left[^{14}\mathrm{C}\right]_0$$
$$\ln 7.82 \approx -1.21 \times 10^{-4}\ t + \ln\left[13.6\right]$$
$$2.057 \approx -1.21 \times 10^{-4}\ t + 2.610$$
$$-0.553 \approx -1.21 \times 10^{-4}\ t$$
$$\therefore \quad t \approx 4570\ years$$

Solution 5: The mass of an oxygen-16 nucleus is 15.990881 amu. What is the binding energy per nucleon, in kJ/nucleon, and per mole of nuclei, in kJ/mol? (The mass of a proton is 1.007276 amu, and the mass of a neutron is 1.008665 amu.)

The reaction is: $8\,{}^{1}_{1}\mathrm{p} + 8\,{}^{1}_{0}\mathrm{n} \longrightarrow {}^{16}_{8}\mathrm{O}$

step 1: weigh the protons and neutrons:

$$\begin{aligned} 8\,{}^{1}_{1}\mathrm{p} &= 8 \times 1.007276\ amu = 8.058208\ amu \\ 8\,{}^{1}_{0}\mathrm{n} &= 8 \times 1.008665\ amu = 8.069320\ amu \\ \text{react} &= \overline{16.127528\ amu} \end{aligned}$$

step 2: find mass defect:

$$\begin{aligned} \Delta m &= 16.127528\ amu - 15.990881\ amu \\ \Delta m &= 0.136647\ amu \end{aligned}$$

and convert amu to kg:

$$0.136647\ amu \times \frac{1\ g}{6.022 \times 10^{23}\ amu} \times \frac{1\ kg}{1000\ g} \approx 2.269 \times 10^{-28}\ kg$$

step 3: Use the Einstein equation to find the total binding energy:

$$\begin{aligned} E &= mc^2 \\ &= 2.269 \times 10^{-28} kg \left(2.998 \times 10^{8}\ m/s\right) 2 \\ E &\approx 2.039 \times 10^{-11}\ J \end{aligned}$$

Nucleon means the particles in the nucleus, the protons and neutrons. Oxygen-16 has 16 nucleons, so divide the total binding energy by 16:

$$\frac{2.039 \times 10^{-11}\ J}{{}^{16}\mathrm{O}} \times \frac{{}^{16}\mathrm{O}}{16\ nucleons} \approx 1.27 \times 10^{-12}\ J/nucleon$$

Use Avogadro's Number to find binding energy per mole:

$$\frac{2.039 \times 10^{-11}\ J}{{}^{16}\mathrm{O}} \times \frac{6.022 \times 10^{23}\ {}^{16}\mathrm{O}}{1\ mol} \approx 1.23 \times 10^{13}\ J/mol$$

Chapter 14: Chemical equilibrium

In CHM 1100, stoichiometry assumes that in a chemical reaction, reactant chemicals change into product chemicals, and that the reaction is complete when as much of the reactants as possible has changed onto products.

This is not entirely correct. (I always say that in CHM 1100, you were a beginner, so we lied to you a lot, in order to keep things simple. In CHM 1200, you're not a beginner anymore, so we'll be lying to you less.)

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reversible reactions and equilibrium

Chemical reactions are REVERSIBLE. Yes, reactants change into products, but the products also change back into reactants at the same time. It's almost like two reactions occurring together. The chemical equation uses a DOUBLE ARROW to indicate the simultaneous forward and reverse changes.

The reaction is "complete" when the rates of the forward and reverse reaction are equal. This is called the reaction EQUILIBRIUM. Be careful: equilibrium does not mean the amount of reactants and products are equal. Most equilibria have one side dominating over the other.

The equilibrium is described by the EQUILIBRIUM EXPRESSION, which is the ratio of products over reactants, measured at equilibrium. Remember, mole ratios are still important – the coefficients of the balanced equation is used as exponents in the expression. The equilibrium expression computes to the EQUILIBRIUM CONSTANT – K. Note, the equilibrium constant is not a mathematical constant – it is not a just number that never changes. The equilibrium constant depends on the specific reaction and the temperature.

If K is very large (much greater than 1), the forward reaction is "favored" over the reverse. If K is very small (much less than 1), the reverse reaction dominates over the forward.

There is a difference between K_c and K_p, because different units can be used to measure the reaction. Subscript "c" means concentration measured in Molarity; subscript "p" means gas pressure measured in atmospheres. Remember: square brackets is the notation for Molarity and P is the symbol for pressure used in equilibrium expressions. Note, although concentrations and pressures have units, we ignore units for the equilibrium constant.

Beware: this unit difference does not mean the equilibrium is somehow different, but it does mean that the numerical values can be different. (Twelve inches is exactly the same as one foot, but the number 1 is different than the number 12.) Since it is a unit difference, you can do a unit conversion, just like in CHM 1100, but normally we use a formula:

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

Remember, in a HETEROGENEOUS EQUILIBRIUM, where the physical phases of the chemicals are not all the same (the word “hetero” means different), we ignore solids and liquids, because the change of the solid and liquid amounts will be very small compared to gas or solution measurements.

Since the equilibrium constant K refers the end of a reaction, we use a different notation for the beginning of the reaction – the REACTION QUOTIENT – Q, which is the ratio of products over reactants, measured with initial values. The beginning of a reaction is different from the end of a reaction – make sure you know whether you have initial or equilibrium values, or both.

If there are no initial products, it is obvious that a reaction will move forward to equilibrium, since there are no products to reverse with. It is also obvious that a reaction will move reverse, if there are no initial reactants. The reaction quotient is most useful determining forward versus reverse, if the the reaction has both initial reactants and products.

If $Q < K$, the reaction shifts FORWARD (to the right, to product side) to equilibrium.

If $Q > K$, the reaction shifts REVERSE (to the left, to reactant side) to equilibrium

If $Q = K$, the reaction is at equilibrium and does not appear to occur.

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the ICE-box

Since the beginning of a reaction is very different from the end of a reaction, you must keep track of initial and equilibrium amounts of the chemicals in a reaction equilibrium. We use a table called the ICE-box to help. Remember, the ICE-box refers to a reaction; it should be written directly under the balanced equation. The ICE box has three rows, labeled “I” for initial amounts of the reaction, “C” for change in amounts during the reaction and "E" for the equilibrium amounts of the reaction. There are also one column for each chemical.

Strictly speaking, the ICE box is bookkeeping, not Chemistry, but since a lot can happen during a reaction, bookkeeping helps keep track of it all.

You are responsible for many variations of equilibrium calculations, especially ICE box calculations – forwards, backwards, upside-down and sideways.

Le Chatelier's Principle

If you "disturb" a chemical reaction that is already at equilibrium, the reaction will shift to new equilibrium amounts to counteract the disturbance.

There are three major types of disturbances and equilibrium shifts.

1: Change amount (concentration, partial pressure) of ONE chemical:
  increase: reaction shifts to OTHER side
  decrease: reaction shifts to SAME side

2: Change total pressure (for gases only)
  increase: reaction shifts to side with FEWER moles of gas
  decrease: reaction shifts to side with GREATER moles of gas
  * changing total volume has OPPOSITE effect (Boyle's Law says gas pressure and volume are INVERSELY proportional)

3: Change temperature (heat):
  endothermic reaction (**Δ**H=pos):
    increase: reaction shifts FORWARD (to the right, to product side)
    decrease: reaction shifts REVERSE (to the left, to reactant side)
  exothermic reaction (**Δ**H=neg):
    increase: reaction shifts REVERSE (to the left, to reactant side)
    decrease: reaction shifts FORWARD (to the right, to product side)

Note: adding catalysts does not shift the equilibrium position, the reaction just reaches equilibrium faster.

Chapter 14: Chemical equilibrium Problems

Problem 1: Write the K_c equilibrium expressions for the following reactions.

(a) $4\ NH_{3\ (g)} + 7\ O_{2\ (g)} \rightleftharpoons 4\ NO_{2\ (g)} + 6\ H_2O_{(g)}$

(b) $HC_2H_3O_{2\ (aq)} \rightleftharpoons H^+_{(aq)} + C_2H_3O^-_{2\ (aq)}$

(c) $2\ N_2O_{5\ (s)} \rightleftharpoons 4\ NO_{2\ (g)} + O_{2\ (g)}$

(d) $3\ NiSO_{4\ (aq)} + 2\ Na_3PO_{4\ (aq)} \rightleftharpoons Ni_3(PO_4)_{2\ (s)} + 3\ Na_2SO_{4\ (aq)}$

Problem 2: Write the K_p equilibrium expressions for the following reactions.

(a) $CS_{2\ (g)} + 4\ H_{2\ (g)} \rightleftharpoons CH_{4\ (g)} + 2\ H_2S_{(g)}$

(b) $2\ KClO_{3\ (s)} \rightleftharpoons 2\ KCl_{(s)} + 3\ O_{2\ (g)}$

(c) $2\ NO_{2\ (g)} \rightleftharpoons N_2O_{4\ (s)}$

Problem 3: In the synthesis of ammonia at 500 °C:

$$N_{2\ (g)} + 3\ H_{2\ (g)} \rightleftharpoons 2\ NH_{3\ (g)}$$

it is observed that the equilibrium concentrations are:

$$\left[NH_3\right] = 9.6 \times 10^{-4}\ M,\ \left[N_2\right] = 7.8 \times 10^{-1}\ M,\ \left[H_2\right] = 2.7 \times 10^{-2}\ M$$

Calculate the values of K_c and K_p for this reaction.

Problem 4: In the formation of nitrosyl chloride at 25 °C:

$$2\ NO_{(g)} + Cl_{2\ (g)} \rightleftharpoons 2\ NOCl_{(g)}$$

the equilibrium pressures are measured as:

$$P_{NOCl} = 1.3\ atm,\ P_{NO} = 4.8 \times 10^{-2}\ atm,\ P_{Cl_2} = 3.3 \times 10^{-1}\ atm$$

Calculate the value of K_p and K_c for this reaction.

Problem 5: Consider the following reaction equilibria at a certain temperature:

$$2\ NO_{2\,(g)} \rightleftharpoons N_2O_{4\,(g)} \qquad K_1 = 8.70$$

$$2\ N_2O_{(g)} + 3\ O_{2\,(g)} \rightleftharpoons 2\ N_2O_{4\,(g)} \qquad K_2 = 73.0$$

Use this information to determine the equilibrium constant for the following reaction:

$$4\ NO_{2\,(g)} \rightleftharpoons 2\ N_2O_{(g)} + 3\ O_{2\,(g)} \quad K_3 = ?$$

Problem 6: Dinitrogen tetroxide gas will decompose to gaseous nitrogen dioxide:

$$N_2O_{4\,(g)} \rightleftharpoons 2\ NO_{2\,(g)}$$

In an experiment, gaseous N_2O_4 was placed in a flask and allowed to reach equilibrium at a temperature where $K_p = 0.133$. At equilibrium, the pressure of N_2O_4 was found to be 2.71 atm. What is the equilibrium pressure of the NO_2?

Problem 7: When sulfur dioxide is oxidized, the reaction is:

$$2\ SO_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2\ SO_{3\,(g)}$$

A 2.00 L flask was filled with 0.0400 mol SO_2 and 0.0200 mol O_2. At equilibrium at 900 K, the flask is found to contain 0.0296 mol SO_3. (a) What is the concentration of each substance in the flask at equilibrium? (b) What is the equilibrium constant, K_c, at 900 K?

Problem 8: In the reaction of carbon monoxide with steam:

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2\,(g)} + H_{2\,(g)}$$

the equilibrium constant, K_c, is 5.10 at 700 K.

If 2.00 mol of each component is mixed into a 5.00 L flask: (a) In which direction will the system will shift to reach equilibrium? (b) What are the equilibrium concentrations of each species?

Problem 9: At a certain temperature, hydrogen and fluorine gases react to produce gaseous hydrogen fluoride:

$$H_{2\,(g)} + F_{2\,(g)} \rightleftharpoons 2\ HF_{(g)} \qquad K_c = 1.15 \times 10^2$$

If 5.00 moles of hydrogen and fluorine gases were added to a 2.00 L flask, calculate the equilibrium concentrations of all species.

Problem 10: At 25 °C, $K_p = 2.9 \times 10^{-3}$ for the reaction:

$$NH_4OCONH_{2\,(s)} \rightleftharpoons 2\ NH_{3\,(g)} + CO_{2\,(g)}$$

During an experiment, some NH_4OCONH_2 is placed in an evacuated reaction flask and allowed to come to equilibrium. What will be the total pressure in the container at equilibrium.

Problem 11: The decomposition equilibrium of nitrosyl bromide is:

$$2\ NOBr_{(g)} \rightleftharpoons 2\ NO_{(g)} + Br_{2\,(g)}$$

If nitrosyl bromide (NOBr) is 34% dissociated at 25 °C and the total pressure is 0.25 atm, calculate K_P for the dissociation at this temperature.

Problem 12: Suppose the reaction system:

$$UO_{2\,(s)} + 4\ HF_{(g)} \rightleftharpoons UF_{4\,(g)} + 2\ H_2O_{(g)}$$

has reached equilibrium. Predict the direction shift that each of the following changes will have on the equilibrium position.

(a) Water vapor is removed.

(b) $UO_{2\,(s)}$ is added to the system.

(c) The volume of the reaction vessel is increased.

Problem 13: Methanol is prepared industrially from synthesis gas (CO and H_2).

$$CO_{(g)} + 2\ H_{2\,(g)} \rightleftharpoons CH_3OH_{(g)} \quad \Delta H^{\circ} = -90.7\ kJ/mol$$

Would the following changes increase or decrease the production of methanol?

(a) The reaction vessel is heated.

(b) Hydrogen gas is added.

(c) The total pressure in the reaction vessel is increased.

Chapter 14: Chemical equilibrium Solutions

Solution 1: Write the K_c equilibrium expressions for the following reactions.

(a) $4\ NH_{3\ (g)} + 7\ O_{2\ (g)} \rightleftharpoons 4\ NO_{2\ (g)} + 6\ H_2O_{(g)}$

$$K_c = \frac{[NO_2]^4\,[H_2O]^6}{[NH_3]^4\,[O_2]^7}$$

(b) $HC_2H_3O_{2\ (aq)} \rightleftharpoons H^+_{(aq)} + C_2H_3O^-_{2\ (aq)}$

$$K_c = \frac{[H^+]\,[C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

(c) $2\ N_2O_{5\ (s)} \rightleftharpoons 4\ NO_{2\ (g)} + O_{2\ (g)}$

$$K_c = [NO_2]^4\,[O_2]$$

(d) $3\ NiSO_{4\ (aq)} + 2\ Na_3PO_{4\ (aq)} \rightleftharpoons Ni_3(PO_4)_{2\ (s)} + 3\ Na_2SO_{4\ (aq)}$

$$K_c = \frac{[Na_2SO_4]^3}{[NiSO_4]^3\,[Na_3PO_4]^2}$$

Solution 2: Write the K_p equilibrium expressions for the following reactions.

(a) $CS_{2\ (g)} + 4\ H_{2\ (g)} \rightleftharpoons CH_{4\ (g)} + 2\ H_2S_{(g)}$

$$K_p = \frac{P_{CH_4}\,{P_{H_2S}}^2}{P_{CS_2}\,{P_{H_2}}^4}$$

(b) $2\ KClO_{3\ (s)} \rightleftharpoons 2\ KCl_{(s)} + 3\ O_{2\ (g)}$

$$K_p = {P_{O_2}}^3$$

(c) $2\ NO_{2\ (g)} \rightleftharpoons N_2O_{4\ (s)}$

$$K_p = \frac{1}{{P_{NO_2}}^2}$$

Solution 3: In the synthesis of ammonia at 500 °C:

$$N_{2\ (g)} + 3\ H_{2\ (g)} \rightleftharpoons 2\ NH_{3\ (g)}$$

it is observed that the equilibrium concentrations are:

$$[NH_3] = 9.6 \times 10^{-4}\ M,\ [N_2] = 7.8 \times 10^{-1}\ M,\ [H_2] = 2.7 \times 10^{-2}\ M$$

Calculate the values of K_c and K_p for this reaction.

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = \frac{[9.6 \times 10^{-4}]^2}{[7.8 \times 10^{-1}]\,[2.7 \times 10^{-2}]^3}$$

$$K_c \approx 6.0 \times 10^{-2}$$

$$\begin{aligned} K_p &= K_c\,(RT)^{\Delta n} \\ &= 6.0 \times 10^{-2}\,(0.0821 \cdot 773)^{-2} \\ &\approx 6.0 \times 10^{-2}\,(63.46)^{-2} \\ &\approx 6.0 \times 10^{-2}\,(2.483 \times 10^{-4}) \end{aligned}$$

$$K_p \approx 1.5 \times 10^{-5}$$

Notice: equilibrium problems often "measure" chemicals individually, out of many in a mixture. This is actually very difficult to do in practical situations. In other words, we are doing pencil-and-paper problems.

Solution 4: In the formation of nitrosyl chloride at 25 °C:

$$2\ NO_{(g)} + Cl_{2\ (g)} \rightleftharpoons 2\ NOCl_{(g)}$$

the equilibrium pressures are measured as:

$$P_{NOCl} = 1.3\ atm,\ P_{NO} = 4.8 \times 10^{-2}\ atm,\ P_{Cl_2} = 3.3 \times 10^{-1}\ atm$$

Calculate the value of K_p and K_c for this reaction.

$$K_p = \frac{{P_{NOCl}}^2}{{P_{NO}}^2\,P_{Cl_2}}$$

$$= \frac{1.3^2}{\left(4.8 \times 10^{-2}\right)^2 \left(3.3 \times 10^{-1}\right)}$$

$$K_p \approx 2.2 \times 10^3$$

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

$$\therefore \quad K_c = \frac{K_p}{(RT)^{\Delta n}}$$

$$= \frac{2.2 \times 10^3}{(0.0821 \cdot 298)^{-1}}$$

$$= 2.2 \times 10^3\,(0.0821 \cdot 298)$$

$$K_c \approx 5.4 \times 10^4$$

Solution 5: Consider the following reaction equilibria at a certain temperature:

$$2\ NO_{2\,(g)} \rightleftharpoons N_2O_{4\,(g)} \qquad K_1 = 8.70$$

$$2\ N_2O_{(g)} + 3\ O_{2\,(g)} \rightleftharpoons 2\ N_2O_{4\,(g)} \qquad K_2 = 73.0$$

Use this information to determine the equilibrium constant for the following reaction:

$$4\ NO_{2\,(g)} \rightleftharpoons 2\ N_2O_{(g)} + 3\ O_{2\,(g)} \qquad K_3 = ?$$

Multiple equilibria similar to Hess' Law, from back in CHM 1100: COMPARE, CORRECT, CANCEL and COMBINE.

Comparing given reaction 1 with the unknown reaction, they have $NO_{2\,(g)}$ in common. However, it is 2 moles in the given, but is 4 moles in the unknown. Reaction 1 needs to be corrected by being multiplied by 2 to match the unknown. Therefore, K_1 must be corrected by taking power of 2 (or squared).

$$4\ NO_{2\,(g)} \rightleftharpoons 2\ N_2O_{4\,(g)} \qquad K_1' = \left(K_1\right)^2 = (8.70)^2 \approx 75.7$$

Comparing given reaction 2 with the unknown reaction, they have $N_2O_{(g)}$ in common. However, it is a reactant in the given, but is a product in the unknown. Reaction 1 needs to be corrected by being reversed to match the unknown. Therefore, K_2 must be corrected by taking inverse.

$$2\ N_2O_{4\,(g)} \rightleftharpoons 2\ N_2O_{(g)} + 3\ O_{2\,(g)} \qquad K_2' = \frac{1}{K_2} = \frac{1}{73.0} \approx 0.0137$$

Looking at the two corrected equations together, there are 2 mol $N_2O_4\ _{(g)}$ on both the reactant and the product sides, and can be cancelled:

$$\begin{array}{llll} 4\ NO_{2\ (g)} & \rightleftharpoons & \cancel{2\ N_2O_{4\ (g)}} & K_1' \approx 75.7 \\ \cancel{2\ N_2O_{4\ (g)}} & \rightleftharpoons & 2\ N_2O_{(g)}\ +\ 3\ O_{2\ (g)} & K_2' \approx 0.0137 \end{array}$$

Looking at what's left, the remaining 4 mol $NO_2\ _{(g)}$ reactant and 2 mol $N_2O_{(g)}$ and 3 mol $O_2\ _{(g)}$ products are added into the correct combined equation, and you get the correct combined equilibrium constant by multiplying the corrected equilibrium constants.

$$4\ NO_{2\ (g)}\ \rightleftharpoons\ 2\ N_2O_{(g)}\ +\ 3\ O_{2\ (g)} \qquad K_3 = K_1' \times K_2' \approx 75.7\,(0.0137)$$

$$K_3 \approx 1.04$$

Solution 6: Dinitrogen tetroxide gas will decompose to gaseous nitrogen dioxide:

$$N_2O_{4\ (g)}\ \rightleftharpoons\ 2\ NO_{2\ (g)}$$

In an experiment, gaseous N_2O_4 was placed in a flask and allowed to reach equilibrium at a temperature where $K_p = 0.133$. At equilibrium, the pressure of N_2O_4 was found to be 2.71 atm. What is the equilibrium pressure of the NO_2?

The ICE-box is not needed, because only equilibrium values are discussed.

$$K_p = \frac{{P_{NO_2}}^2}{P_{N_2O_4}}$$

$$\therefore \quad P_{NO_2} = \sqrt{K_p\ P_{N_2O_4}}$$

$$= \sqrt{0.133\,(2.71)}$$

$$P_{NO_2} = 0.600\ atm$$

Solution 7: When sulfur dioxide is oxidized, the reaction is:

$$2\ SO_{2\ (g)}\ +\ O_{2\ (g)}\ \rightleftharpoons\ 2\ SO_{3\ (g)}$$

A 2.00 L flask was filled with 0.0400 mol SO_2 and 0.0200 mol O_2. At equilibrium at 900 K, the flask is found to contain 0.0296 mol SO_3. (a) What is the concentration of each substance in the flask at equilibrium? (b) What is the equilibrium constant, K_c, at 900 K?

(a) Pay attention to the units – concentrations are in Molarity, not the number of moles. In CHM 1200, you are always responsible for proper units – you will not be reminded.

Initial reactant concentrations are:

$$[SO_2]_0 = \frac{0.0400\ mol}{2.00\ L} = 0.0200\ M$$

$$[O_2]_0 = \frac{0.0200\ mol}{2.00\ L} = 0.0100\ M$$

Initial product concentration is not mentioned. Assume it is zero, which is the normal situation.

Equilibrium product concentration can be found from given moles:

$$[SO_3] = \frac{0.0296\ mol}{2.00\ L} = 0.0148\ M$$

An ICE-box is needed, because the initial and equilibrium values must be kept separate. Since there are no initial products, the reaction will move forward. Forward change has a decrease of reactants and increase of products. Since the Change during the reaction is unknown, just call it variable "x" – straight out of Math class. Remember, since this is Chemistry, the stoichiometric mole ratio still applies to the Change values.

	$2\ \mathbf{SO_2}_{\,(g)}$ +	$\mathbf{O_2}_{\,(g)}$ ⇌	$2\ \mathbf{SO_3}_{\,(g)}$
I	0.0200 M	0.0100 M	0
C	– 2x	– x	+ 2x
E	0.0200 M – 2x	0.0100 M – x	0.0148 M

Notice that the Initial and Equilibrium SO_3 concentrations are both known. Therefore the SO_3 Change can be immediately found; "x" is not truly unknown.

$$\begin{aligned} SO_3 \quad I + C &= E \\ 0 + 2x &= 0.0148\ M \\ \therefore \quad x &= \frac{0.0148\ M}{2} \\ x &= 0.0074\ M \end{aligned}$$

Use "x" to find reactant equilibrium concentrations:

$$[SO_2] = 0.0200 - 2x = 0.0200 + 2\,(0.0074) = 0.0052\ M$$

$$[O_2] = 0.0100 - x = 0.0100 + 0.0074 = 0.0026\ M$$

(b) Use equilibrium expression:

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

$$= \frac{[0.0148]^2}{[0.0052]^2\,[0.0026]}$$

$$K_c \approx 3.1 \times 10^3$$

Solution 8: In the reaction of carbon monoxide with steam:

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2\,(g)} + H_{2\,(g)}$$

the equilibrium constant, K_c, is 5.10 at 700 K.

If 2.00 mol of each component is mixed into a 5.00 L flask: (a) In which direction will the system will shift to reach equilibrium? (b) What are the equilibrium concentrations of each species?

(a) given: all initial concentrations $= \dfrac{2.00\ mol}{5.00\ L} = 0.400\ M$

unknown: find Q and compare with K

$$Q_c = \frac{[CO_2]_0\,[H_2]_0}{[CO]_0\,[H_2O]_0}$$

$$= \frac{[0.400]\,[0.400]}{[0.400]\,[0.400]}$$

$$Q_c = 1$$

since Q < K, the reaction shifts FORWARD, to the right, to more products

(b) given: all initial concentrations $= \dfrac{2.00\ mol}{5.00\ L} = 0.400\ M$

unknown: all equilibrium concentrations

Need ICE-box, because the Initial is different than the Equilibrium.

Forward Change has decrease of reactants and increase of products.

	$CO_{(g)}$	+ $H_2O_{(g)}$	⇌ $CO_{2\,(g)}$	+ $H_{2\,(g)}$
I	0.400 M	0.400 M	0.400 M	0.400 M
C	– x	– x	+ x	+ x
E	0.400 M – x	0.400 M – x	0.400 M + x	0.400 M + x

When the ICE-box is complete, transfer the equilibrium values into the equilibrium expression and “solve for x”:

$$K_c = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]}$$

$$5.10 = \frac{[0.400 + x]\,[0.400 + x]}{[0.400 - x]\,[0.400 - x]}$$

$$5.10 = \frac{[0.400 + x]^2}{[0.400 - x]^2}$$

$$\sqrt{5.10} = \sqrt{\frac{[0.400 + x]^2}{[0.400 - x]^2}}$$

$$2.258 \approx \frac{0.400 + x}{0.400 - x}$$

$$2.258\,(0.400 - x) \approx 0.400 + x$$

$$0.9032 - 2.258x \approx 0.400 + x$$

$$0.5032 \approx 3.258x$$

$$\therefore \quad x \approx 0.154\ M$$

Be careful, although equilibrium calculations can be long, this is not a Math class. Solving for “x” does not mean you’ve finished the Chemistry.

$$[CO_2] = [H_2] = 0.400 + x = 0.400 + 0.154 = 0.554\ M$$

$$[CO] = [H_2O] = 0.400 - x = 0.400 - 0.154 = 0.246\ M$$

Notice the temperature is not used in ICE-box calculations.

Solution 9: At a certain temperature, hydrogen and fluorine gases react to produce gaseous hydrogen fluoride:

$$H_{2\,(g)} \;+\; F_{2\,(g)} \;\rightleftharpoons\; 2\ HF_{(g)} \qquad K_c = 1.15 \times 10^2$$

If 5.00 moles of hydrogen and fluorine gases were added to a 2.00 L flask, calculate the equilibrium concentrations of all species.

given: initial reactant concentrations are: $[H_2]_0 = [F_2]_0 = \dfrac{5.00\ mol}{2.00\ L} = 2.50\ M$

unknown: all equilibrium concentrations

Set up ICE-box:

	$\mathbf{H_2}_{\,(g)}$ +	$\mathbf{F_2}_{\,(g)}$ ⇌	2 $\mathbf{HF}_{(g)}$
I	2.50 M	2.50 M	0
C	– x	– x	+ 2x
E	2.50 M – x	2.50 M – x	2x

Transfer the equilibrium values into the equilibrium expression and “solve for x”:

$$K_c = \frac{[H_2]^2}{[H_2]\,[F_2]}$$

$$1.15 \times 10^2 = \frac{[2x]^2}{[2.50 - x]^2}$$

$$\sqrt{1.15 \times 10^2} = \sqrt{\frac{[2x]^2}{[2.50 - x]^2}}$$

$$10.72 \approx \frac{2x}{2.50 - x}$$

$$10.72\,(2.50 - x) \approx 2x$$

$$26.81 - 10.72x \approx 2x$$

$$26.81 \approx 12.72x$$

$$\therefore \quad x \approx 2.11\ M$$

Use "x" to finish the Chemistry

$$[H_2] = [F_2] = 2.50\ M - x = 2.50\ M - 2.11\ M = 0.39\ M$$
$$[HF] = 2x = 2(2.11\ M) = 4.22\ M$$

Solution 10: At 25 °C, $K_p = 2.9 \times 10^{-3}$ for the reaction:

$$NH_4OCONH_{2\,(s)} \rightleftharpoons 2\ NH_{3\,(g)} + CO_{2\,(g)}$$

During an experiment, some NH_4OCONH_2 is placed in an evacuated reaction flask and allowed to come to equilibrium. What will be the total pressure in the container at equilibrium.

Notice the heterogeneous phases. The NH_4OCONH_2 is a solid – ignore it in the equilibrium calculations!

ICE-box:

	$NH_4OCONH_{2\,(s)}$ $\rightleftharpoons$	**2 $NH_{3\,(g)}$** +	**$CO_{2\,(g)}$**
I		0	0
C		+ 2x	+ x
E		2x	x

Equilibrium expression:

$$K_p = P_{NH_3}{}^2\ P_{CO_2}$$
$$2.9 \times 10^{-3} = (2x)^2 (x)$$
$$= \left(4x^2\right)(x)$$
$$2.9 \times 10^{-3} = 4x^3$$
$$7.25 \times 10^{-4} = x^3$$
$$\therefore \quad x = \sqrt[3]{7.25 \times 10^{-4}}$$
$$x \approx 9.0 \times 10^{-2}\ atm$$

Find equilibrium pressures:

$$P_{NH_3} = 2x = 2\left(9.0 \times 10^{-2} atm\right) \approx 0.18\ atm$$

$$P_{CO_2} = x \approx 0.090\ atm$$

Use Dalton's Law to find total pressure:

$$\begin{aligned} P_{total} &= P_{NH_3} + P_{CO_2} \\ &= 0.18\ atm + 0.090\ atm \\ P_{total} &= 0.27\ atm \end{aligned}$$

Solution 11: The decomposition equilibrium of nitrosyl bromide is:

$$2\ \mathrm{NOBr}_{(g)} \rightleftharpoons 2\ \mathrm{NO}_{(g)} + \mathrm{Br}_{2\ (g)}$$

If nitrosyl bromide (NOBr) is 34% dissociated at 25 °C and the total pressure is 0.25 atm, calculate K_P for the dissociation at this temperature.

This problem is unusual because all individual pressures are unknown. However, the problem does say "34% dissociated." That means the Initial amount of NOBr = 100%, the Change of NOBr = 34%, and the ICE-box can be written as:

	2 NOBr$_{(g)}$ ⇌	**2 NO**$_{(g)}$ +	**Br**$_{2\ (g)}$
I	100%	0	0
C	– 34%	+ 34%	+ 17%
E	66%	34%	17%

So Dalton's Law tell us:

$$\begin{aligned} P_{total} &= P_{NOBr} + P_{NO} + P_{Br_2} \\ 0.25\ atm &= 66\% + 34\% + 17\ \% \\ 0.25\ atm &= 117\ \% \\ \therefore \quad 100\ \% &\approx 0.214\ atm \end{aligned}$$

And the ICE-box can be rewritten:

	2 NOBr$_{(g)}$ ⇌	**2 NO**$_{(g)}$ +	**Br**$_{2\ (g)}$
I	0.214 atm	0	0
C	– 0.073 atm	+ 0.073 atm	+ 0.036 atm
E	0.141 atm	0.073 atm	0.036 atm

Equilibrium expression:

$$K_p = \frac{P_{NO}{}^2 \; P_{Br_2}}{P_{NOBr}{}^2}$$

$$K_p = \frac{0.073^2 \;\left(0.036\right)}{0.141^2}$$

$$K_p \approx 9.6 \times 10^{-3}$$

Solution 12: Suppose the reaction system:

$$UO_{2\,(s)} \; + \; 4\ HF_{(g)} \; \rightleftharpoons \; UF_{4\,(g)} \; + \; 2\ H_2O_{(g)}$$

has reached equilibrium. Predict the direction shift that each of the following changes will have on the equilibrium position.

(a) Water vapor is removed.

FORWARD SHIFT (Less water vapor product causes shift toward the water.)

(b) $UO_{2\,(s)}$ is added to the system.

NO EFFECT (Solids do not effect equilibrium.)

(c) The volume of the reaction vessel is increased.

REVERSE SHIFT (Greater volume shifts toward higher 4 gas moles reactant side.)

Solution 13: Methanol is prepared industrially from synthesis gas (CO and H_2).

$$CO_{(g)} \; + \; 2\ H_{2\,(g)} \rightleftharpoons \; CH_3OH_{(g)} \quad \Delta H^{\circ} = -90.7\ kJ/mol$$

Would the following changes increase or decrease the production of methanol?

(a) The reaction vessel is heated.

DECREASE (More heat increases temperature, which causes reverse shift on an exothermic reaction, away from the methanol product.)

(b) Hydrogen gas is added.

INCREASE (More hydrogen reactant causes shift away from the hydrogen and toward the methanol product.)

(c) The total pressure in the reaction vessel is increased.

INCREASE (Higher pressure shifts toward lower 1 gas moles product side, which is the methanol.)

Chapter 15: Acid-base equlibria

Recall: Acids and bases were introduced in CHM 1100. However, the acid/base concepts used in CHM 1100 are incomplete. (In CHM 1100, we lied to you a lot, in order to keep things simple. In CHM 1200, we lie to you less.)

Brønsted acids and bases

We use the Brønsted explanation of acids and bases in CHM 1200. Acids and bases do not simply dissociate when dissolved in water, becoming electrolytes in aqueous solutions.

According to Brønsted, an acid reacts with water, by donating a proton (equivalent to a hydrogen ion, H^+) to the water, producing an anion and a hydronium ion (H_3O^+). Hydronium ion is the equivalent to hydrogen ion dissociated by a CHM 1100 acid.

A molecular base reacts with water, by accepting a proton from the water, producing a cation and a hydroxide ion (OH^-). During a neutralization reaction, the acid donates a proton to the base, which accepts it.

In other words, all acid/base reactions are PROTON TRANSFER REACTIONS.

In addition, Brønsted accounts for reversible reactions. Since an acid donates a proton to produce an anion in the forward reaction, the anion must be a base because it accepts a proton in the reverse reaction – its conjugate base. And, since a base accepts a proton to produce a cation in the forward reaction, the cation must be an acid because it donates a proton in the reverse reaction – its conjugate acid. Ions are not just electrolytes floating around in the water. In other words, all acids and bases are part of a CONJUGATE ACID-BASE PAIR.

$$\mathrm{HA}_{(aq)} + \mathrm{H_2O}_{(l)} \rightleftharpoons \mathrm{A}^-_{(aq)} + \mathrm{H_3O}^+_{(aq)}$$

where HA is a generic acid and A^- is its conjugate base.

$$\mathrm{B}_{(aq)} + \mathrm{H_2O}_{(l)} \rightleftharpoons \mathrm{BH}^+_{(aq)} + \mathrm{OH}^-_{(aq)}$$

where B is a generic base and BH^+ is its conjugate acid.

Note, since acids and bases are carefully defined, you are responsible for recognizing acids and bases, and for writing all acid or base chemical equations. Reactions will not be given in this topic. Remember, this is not a Math class. If you don't know the chemical reaction, you have nothing to calculate.

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strong versus weak acids and bases.

A strong acid has 100% ionization (to use CHM 1100 vocabulary), or complete dissociation, or no real equilibrium.

There are only a small number of strong acids. Memorize them!

HCl	hydrochloric
HNO_3	nitric
$HClO_4$	perchloric
H_2SO_4	sulfuric
HBr	hydrobromic
HI	hydroiodic

A weak acid has less than 100% ionization (to use CHM 1100 vocabulary), or incomplete dissociation, or a real equilibrium. Since weak acids have an equilibrium, they also have an equilibrium expression and constant - K_a - with subscript "a" for acid, that usually looks like this:

$$\mathrm{HA}_{(aq)} + \mathrm{H_2O}_{(l)} \rightleftharpoons \mathrm{A}^-_{(aq)} + \mathrm{H_3O}^+_{(aq)} \quad K_a = \frac{[\mathrm{A}^-]\left[\mathrm{H_3O}^+\right]}{[\mathrm{HA}]}$$

There are hundreds of weak acids. You are not expected to memorize them. In this class, any acid that is not on the above list of strong acids is weak, unless you are specifically told otherwise.

Note, our weak acids will usually be very weak - less than 5% ionization.

The most famous weak acid is acetic acid, $HC_2H_3O_2$, with $K_a = 1.8 \times 10^{-5}$.

$$\mathrm{HC_2H_3O_2}_{\,(aq)} + \mathrm{H_2O}_{(l)} \rightleftharpoons \mathrm{C_2H_3O_2^-}_{\,(aq)} + \mathrm{H_3O}^+_{(aq)} \quad K_a = 1.8 \times 10^{-5}$$

Since you'll be using acetic acid a lot, memorizing this reaction might be helpful.

Special note: acetic acid is an "organic acid". Carbon the important element in organic chemistry, and the chemical formulae of organic compounds put the carbon first. In chemistry, acetic acid is written CH_3COOH. The donated proton is the last hydrogen, so the reaction can be written:

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)} \quad K_a = 1.8 \times 10^{-5}$$

Note, it is simpler to write weak acid equilibria as a Arrhenius dissociation like in CHM 1100, not a Brønsted proton transfer:

$$HC_2H_3O_{2\,(aq)} \rightleftharpoons H^+_{(aq)} + C_2H_3O^-_{2\,(aq)} \quad K_a = 1.8 \times 10^{-5}$$

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)} \quad K_a = 1.8 \times 10^{-5}$$

Some professors do. It does not matter for calculations, but you must recognize the conceptual difference. The Arrhenius dissociation is known to be incorrect, atom-by-atom and molecule-by-molecule.

The concept of strong and weak bases is similar. Strong bases have 100% ionization, or complete dissociation, or no real equilibrium. Any Group 1A or 2A hydroxide is considered a strong ionic base; normally written as a simple Arrhenius dissociation like in CHM 1100, not a Brønsted proton transfer.

Weak bases have less than 100% ionization, or incomplete dissociation, or a real equilibrium; with an equilibrium expression and constant - K_b - with subscript "b" for base, looking like this.

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)} \quad K_b = \frac{\left[BH^+\right][OH^-]}{[B]}$$

The most famous weak base is ammonia, NH_3 , with $K_b = 1.8 \times 10^{-5}$.

Note, the fact that the K_a of acetic acid and K_b of ammonia have the same numerical value is purely a coincidence. Don't read anything into it. Note also, ammonia is a molecular base. Its base behavior cannot be understood under the Arrhenius model. Ammonia's reaction must be written as a Brønsted reaction.

$$NH_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons NH^+_{4\,(aq)} + OH^-_{(aq)} \quad K_b = 1.8 \times 10^{-5}$$

Since you'll be using ammonia a lot, you should memorize this reaction.

Brønsted-only acids and bases

The Brønsted model of acids and bases is much "looser" than the Arrhenius model. Many acids and bases cannot be explained by Arrhenius, but are obvious under Brønsted.

Salt solutions are not necessarily neutral, because ions are not just electrolytes floating around in the water. Some salts are acidic; others are basic, depending on the conjugate ion. Any salt of a weak acid will be basic, because the anion is its conjugate base. Any salt of a weak base will be acidic, because the cation is its conjugate base. (Remember, conjugates are opposites.) Only salts of strong acids and bases are neutral.

Since water is a highly polar molecule, they have interesting interactions with other charged species. For example, 3+ and 2+ cations tend to attract the negative oxygen pole of water molecules, leaving the positive hydrogen poles likely to dissociate - hydrated cations are acids. The most famous are iron(III) and aluminum hydrates - $\mathrm{Fe}\,(\mathrm{H_2O})_6^{3+}$ and $\mathrm{Al}\,(\mathrm{H_2O})_6^{3+}$.

$$\mathrm{Al}\,(\mathrm{H_2O})^{3+}_{6\,(aq)} \; + \; \mathrm{H_2O}_{(l)} \; \rightleftharpoons \; \mathrm{Al}\,(\mathrm{H_2O})_5\,\mathrm{OH}^{2+}_{(aq)} \; + \; \mathrm{H_3O}^{+}_{(aq)} \quad K_a = 1.4 \times 10^{-5}$$

the pH scale

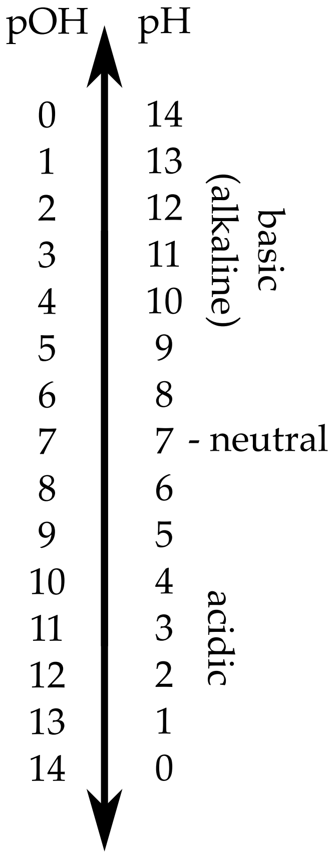
"Strong" does not mean the same as "powerful" when we talk about acids and bases.

Since both the acid concentration and its equilibrium affects the hydrogen ion concentration of acid solutions, the corrosive power or "dangerous-ness," of acids is compared on the pH scale.

The higher the hydrogen ion concentration, the lower the pH, and vice versa.

The pH scale normally ranges between 0 and 14 (at 25 °C), although it can go beyond these limits. You are not expected to memorize the specific pH values of chemicals, except that pH 7 is neutral, less than pH 7 is acidic and greater than pH 7 is basic. Pure water is neutral. Distilled water is pure. Beware, rain water, tap water, bottled water, etc. are not pure.

The formula for pH is: $\mathrm{pH} = -\log\left[\mathrm{H^+}\right]$



pH is an abbreviation for “power of hydrogen” and “log” is the abbreviation for “common logarithm.” Remember how to use logarithms on your scientific calculator. Notice, we are using “common log” in this chapter. Don’t mix up “common log” with “natural log” used during Kinetics.

The concept of the caustic power of bases is similar: the base concentration and its equilibrium affects the hydroxide ion concentration of base solutions, but is measured on the pOH scale.

The higher the hydroxide ion concentration, the lower the pOH, and vice versa.

The pOH scale also ranges between 0 and 14 (at 25 °C), but opposite the pH scale – pOH 7 is neutral, less than pOH 7 is basic and greater than pOH 7 is acidic. A strong acid may be called a weak base, and vice versa.

Notice: pH + pOH = 14

The formula for pOH is: $\mathrm{pOH} = -\log\,[\mathrm{OH}^-]$

Since your calculator does the the work, finding pH or pOH from hydrogen or hydroxide concentration is simple. The difficulty is determining the hydrogen or hydroxide concentration by stoichiometry (for strong acids or bases) or equilibrium calculation (for weak acids or bases).

Remember, our weak acids and bases are usually very weak. Therefore, we normally use the 5% rule approximation to avoid a tedious quadratic equation calculation.

We will be doing a lot of acid and base equilibrium problems, because acids and bases are very common and important chemicals.

Chapter 15: Acid-base equlibria Problems

Problem 1: Write the equilibrium reaction and the equilibrium expression for the following weak acids:

(a) HCN

(b) HSO_4^-

(c) $CH_3NH_3^+$

Problem 2: Write the equilibrium reaction and the equilibrium expression for the following weak bases:

(a) CH_3NH_2

(b) HPO_4^{2-}

Problem 3: In the following reactions, identify the acid, the base, the conjugate base, and the conjugate acid.

(a) $HOCl_{(aq)} + C_5H_5N_{(aq)} \rightleftharpoons OCl^-_{(aq)} + C_5H_5NH^+_{(aq)}$

(b) $HPO^{2-}_{4\ (aq)} + CO^{2-}_{3\ (aq)} \rightleftharpoons PO^{3-}_{4\ (aq)} + HCO^-_{3\ (aq)}$

(c) $HCO^-_{3\ (aq)} + NH^+_{4\ (aq)} \rightleftharpoons H_2CO_{3\ (aq)} + NH_{3\ (aq)}$

Problem 4: What is the pH of (a) a 0.20 M HNO_3 solution, and (b) a 0.20 M HNO_2 solution ($K_a = 4.0 \times 10^{-4}$)?

Problem 5: What is the pH of a 0.025 M $Ba(OH)_2$ solution?

Problem 6: What is the pH of a 0.025 M NH_3 solution? ($K_b = 1.8 \times 10^{-5}$)

Problem 7: The pH of a 0.063 M solution of hypobromous acid (HOBr) is 4.95. Calculate K_a.

Problem 8: Vinegar is a solution of acetic acid. Food-grade vinegar typically has a pH of 3.0. Since K_a (acetic acid) $= 1.8 \times 10^{-5}$, what is the molar concentration of vinegar?

Problem 9: Calculate is the pH of a 0.20 M NaF solution? K_a (HF) $= 7.2 \times 10^{-4}$.

Chapter 15: Acid-base equlibria Solutions

Solution 1: Write the equilibrium reaction and the equilibrium expression for the following weak acids:

(a) HCN

$$HCN_{(aq)} + H_2O_{(l)} \rightleftharpoons CN^-_{(aq)} + H_3O^+_{(aq)} \quad K_a = \frac{[CN^-]\left[H_3O^+\right]}{[HCN]}$$

(b) HSO_4^-

$$HSO^-_{4\,(aq)} + H_2O_{(l)} \rightleftharpoons SO^{2-}_{4\,(aq)} + H_3O^+_{(aq)} \quad K_a = \frac{\left[SO_4^{2-}\right]\left[H_3O^+\right]}{\left[HSO_4^-\right]}$$

(c) $CH_3NH_3^+$

$$CH_3NH^+_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons CH_3NH_{2\,(aq)} + H_3O^+_{(aq)} \quad K_a = \frac{\left[CH_3NH_2\right]\left[H_3O^+\right]}{\left[CH_3NH_3^+\right]}$$

Solution 2: Write the equilibrium reaction and the equilibrium expression for the following weak bases:

(a) CH_3NH_2

$$CH_3NH_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons CH_3NH^+_{3\,(aq)} + OH^-_{(aq)} \quad K_b = \frac{\left[CH_3NH_3^+\right][OH^-]}{\left[CH_3NH_2\right]}$$

(b) HPO_4^{2-}

$$HPO^{2-}_{4\,(aq)} + H_2O_{(l)} \rightleftharpoons H_2PO^-_{4\,(aq)} + OH^-_{(aq)} \quad K_b = \frac{\left[H_2PO_4^-\right][OH^-]}{\left[HPO_4^{2-}\right]}$$

Solution 3: In the following reactions, identify the acid, the base, the conjugate base, and the conjugate acid.

(a) $HOCl_{(aq)} + C_5H_5N_{(aq)} \rightleftharpoons OCl^-_{(aq)} + C_5H_5NH^+_{(aq)}$

Since the H^+ transfers from HOCl to C_5H_5N in the forward reaction, the acid is HOCl, the base is C_5H_5N, the conjugate base is OCl^-, and the conjugate acid is $C_5H_5NH^+$.

(b) $HPO^{2-}_{4\ (aq)} + CO^{2-}_{3\ (aq)} \rightleftharpoons PO^{3-}_{4\ (aq)} + HCO^-_{3\ (aq)}$

Since the H^+ forward transfer is from HPO_4^{2-} to CO_3^{2-}, the acid is HPO_4^{2-}, the base is CO_3^{2-}, the conjugate base is PO_4^{3-}, and the conjugate acid is HCO_3^-.

(c) $HCO^-_{3\ (aq)} + NH^+_{4\ (aq)} \rightleftharpoons H_2CO_{3\ (aq)} + NH_{3\ (aq)}$

Since the H^+ transfers from NH_4^+ to HCO_3^-, the acid is NH_4^+, the base is HCO_3^-, the conjugate base is NH_3 , and the conjugate acid is H_2CO_3 .

Solution 4: What is the pH of (a) a 0.20 M HNO_3 solution, and (b) a 0.20 M HNO_2 solution ($K_a = 4.0 \times 10^{-4}$)?

(a) Nitric acid is a strong acid. Its reaction is simple as a dissociation, and its hydrogen ion concentration can be found using simple a 1-to-1 mole ratio stoichiometry.

$\mathbf{HNO_{3\ (aq)}}$	$\longrightarrow$	$\mathbf{H^+_{(aq)}}$	+	$\mathbf{NO^-_{3\ (aq)}}$
0.20 *M*	$\longrightarrow$	0.20 *M*	+	0.20 *M*

Now just use the pH formula:

$$\begin{aligned} pH &= -\log\left[H^+\right] \\ pH &= -\log\left[0.20\right] \\ &\approx -(-0.70) \\ pH &\approx 0.70 \end{aligned}$$

(b) Nitrous acid is a weak acid. Finding its hydrogen ion concentration requires using an ICE-box equilibrium calculation. Remember the water has a heterogenous phase.

	$HNO_{2\,(aq)}$	+ $H_2O_{(aq)}$ ⇌	$NO_{2\,(aq)}^-$	+ $H_3O^+_{(aq)}$
I	0.20 M		0	0
C	– x		+ x	+ x
E	0.20 M – x		x	x

Equilibrium expression:

$$K_a = \frac{\left[NO_2^-\right]\left[H_3O^+\right]}{\left[HNO_2\right]}$$

$$4.0 \times 10^{-4} = \frac{x^2}{0.20 - x}$$

using the 5% rule approximation

$$4.0 \times 10^{-4} \approx \frac{x^2}{0.20}$$

$$8.0 \times 10^{-5} \approx x^2$$

$$\therefore \quad x \approx \sqrt{8.0 \times 10^{-5}}$$

$$x \approx 8.94 \times 10^{-3}\ M = \left[H_3O^+\right] \equiv \left[H^+\right]$$

Since all weak acids have similar ICE-boxes and equilibrium expressions, some people skip to the 5% rule approximation. I don't, because I don't like to hide the Chemistry.

Compute pH:

$$\begin{aligned} pH &= -\log\left[H^+\right] \\ pH &= -\log\left[8.94 \times 10^{-3}\right] \\ &\approx -\left(-2.05\right) \\ pH &\approx 2.05 \end{aligned}$$

Solution 5: What is the pH of a 0.025 M $Ba(OH)_2$ solution?

Barium hydroxide is a strong ionic base. Its reaction is written as a simple dissociation, and its hydroxide ion concentration is found using a stoichiometry calculation. Beware, it has a 1-to-2 mole ratio.

$\mathbf{Ba(OH)_2}_{\ (aq)}$	$\longrightarrow$	$\mathbf{Ba}^{2+}_{(aq)}$	$+$	$2\ \mathbf{OH}^{-}_{(aq)}$
$0.025\ M$	$\longrightarrow$	$0.025\ M$	$+$	$0.050\ M$

Bases do not produce hydrogen ions directly, and their pH cannot be computed directly. Find the pOH first:

$$\begin{aligned} \text{pOH} &= -\log\,[\text{OH}^-] \\ \text{pOH} &= -\log\left[0.050\right] \\ &\approx -(-1.30) \\ \text{pOH} &\approx 1.30 \end{aligned}$$

Then convert to pH:

$$\begin{aligned} \text{pH} + \text{pOH} &= 14 \\ \therefore \quad \text{pH} &= 14 - \text{pOH} \\ &\approx 14 - 1.30 \\ \text{pH} &\approx 12.70 \end{aligned}$$

Solution 6: What is the pH of a 0.025 M NH_3 solution? ($K_b = 1.8 \times 10^{-5}$)

$$NH_{3\ (aq)} + H_2O_{(l)} \rightleftharpoons NH^+_{4\ (aq)} + OH^-_{(aq)}$$

Since ammonia is a weak base, finding its hydroxide ion concentration requires using an ICE-box equilibrium calculation.

	$\mathbf{NH_3}_{\ (aq)}$	$+$ $\mathbf{H_2O}_{(l)}$ $\rightleftharpoons$	$\mathbf{NH_4^+}_{\ (aq)}$	$+$ $\mathbf{OH}^-_{(aq)}$
I	0.025 M		0	0
C	– x		+ x	+ x
E	0.025 M – x		x	x

Equilibrium expression:

$$K_b = \frac{\left[\mathrm{NH_4^+}\right]\left[\mathrm{OH^-}\right]}{\left[\mathrm{NH_3}\right]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.025 - x}$$

using the 5% rule approximation

$$1.8 \times 10^{-5} \approx \frac{x^2}{0.025}$$

$$4.5 \times 10^{-7} \approx x^2$$

$$\therefore \quad x \approx \sqrt{4.5 \times 10^{-7}}$$

$$x \approx 6.71 \times 10^{-4}\ M = [\mathrm{OH^-}]$$

Since all weak bases have similar ICE-boxes and equilibrium expressions, some people skip to the 5% rule approximation. I don't, because I don't like to hide the Chemistry.

For any base, use the hydroxide concentration to find the pOH first, and then convert to pH:

$$\mathrm{pOH} = -\log\,[\mathrm{OH^-}]$$

$$\mathrm{pOH} = -\log\left[6.71 \times 10^{-4}\right]$$

$$\approx -(-3.17)$$

$$\mathrm{pOH} \approx 3.17$$

$$\mathrm{pH} + \mathrm{pOH} = 14$$

$$\therefore \quad \mathrm{pH} = 14 - \mathrm{pOH}$$

$$\approx 14 - 3.17$$

$$\mathrm{pH} \approx 10.83$$

Solution 7: The pH of a 0.063 M solution of hypobromous acid (HOBr) is 4.95. Calculate K_a.

Notice this problem is "backwards". It gives the pH and asks for K_a. Therefore, begin with the pH formula to find the hydrogen ion concentration:

$$\mathrm{pH} = -\log\left[\mathrm{H^+}\right]$$

$$-\mathrm{pH} = \log\left[\mathrm{H^+}\right]$$

$$\therefore \quad \left[\mathrm{H^+}\right] = 10^{\,\text{-pH}}$$

$$= 10^{-4.95}$$

$$\left[\mathrm{H_3O^+}\right] \equiv \left[\mathrm{H^+}\right] \approx 1.12 \times 10^{-5}$$

Now, go back to the ICE-box:

	$\mathbf{HOBr}_{(aq)}$	+ $\mathbf{H_2O}_{(aq)}$	$\rightleftharpoons$ $\mathbf{OBr}^-_{(aq)}$	+ $\mathbf{H_3O}^+_{(aq)}$
I	0.063 M		0	0
C	− x		+ x	+ x
E	0.063 M − x		x	1.12×10^{-5} M

At this point, you need to notice that the Initial and Equilibrium H_3O^+ concentrations are both known. Therefore "x" is not truly unknown.

$$H_3O^+ \quad I + C = E$$
$$0 + x = 1.12 \times 10^{-5}\ M$$
$$\therefore \quad x = 1.12 \times 10^{-5}\ M$$

Use "x" to find the other equilibrium concentrations:

$$[\text{HOBr}] = 0.063 - x = 0.063 - 1.12 \times 10^{-5} \approx 0.063\ M$$

$$[\text{OBr}^-] = x = 1.12 \times 10^{-5}\ M$$

Equilibrium expression:

$$K_a = \frac{[\text{OBr}^-]\left[\text{H}_3\text{O}^+\right]}{[\text{HOBr}]}$$

$$K_a = \frac{\left(1.12 \times 10^{-5}\right)^2}{0.063}$$

$$K_a \approx 2.0 \times 10^{-9}$$

Solution 8: Vinegar is a solution of acetic acid. Food-grade vinegar typically has a pH of 3.0. Since K_a (acetic acid) $= 1.8 \times 10^{-5}$, what is the molar concentration of vinegar?

This problem is also "backwards". It gives the pH and asks for initial concentration. Therefore, begin by using the pH formula to find the hydrogen ion concentration:

$$\text{pH} = -\log\left[\text{H}^+\right]$$
$$-\text{pH} = \log\left[\text{H}^+\right]$$
$$\therefore \quad \left[\text{H}^+\right] = 10^{\text{-pH}}$$
$$= 10^{-3.0}$$
$$\left[\text{H}_3\text{O}^+\right] \equiv \left[\text{H}^+\right] = 1.0 \times 10^{-3}$$

Back to the ICE-box. Since the Initial acetic acid concentration is unknown, you need a variable. I just use "y", because "x" is used for Change values.

	$HC_2H_3O_2\,_{(aq)}$ +	$H_2O_{(l)}$ ⇌	$C_2H_3O_2^-\,_{(aq)}$ +	$H_3O^+_{(aq)}$
I	y		0	0
C	– x		+ x	+ x
E	y – x		x	1.0×10^{-3} M

Notice that the Initial and Equilibrium hydronium concentrations are both known. Therefore the H_3O^+ Change can be immediately found; "x" is not truly unknown.

$$H_3O^+ \quad I + C = E$$
$$0 + x = 1.0 \times 10^{-3}\ M$$
$$\therefore \quad x = 1.0 \times 10^{-3}\ M$$

And the ICE-box can be rewritten as:

	$HC_2H_3O_2\,_{(aq)}$ +	$H_2O_{(l)}$ ⇌	$C_2H_3O_2^-\,_{(aq)}$ +	$H_3O^+_{(aq)}$
I	y		0	0
C	– 1.0×10^{-3}		+ 1.0×10^{-3}	+ 1.0×10^{-3}
E	y – 1.0×10^{-3} M		1.0×10^{-3} M	1.0×10^{-3} M

Equilibrium expression:

$$K_a = \frac{[C_2H_3O_2^-]\,[H_3O^+]}{[HC_2H_3O_2]}$$
$$1.8 \times 10^{-5} = \frac{(1.0 \times 10^{-3})^2}{y - 1.0 \times 10^{-3}}$$
$$1.8 \times 10^{-5}\,(y - 1.0 \times 10^{-3}) = (1.0 \times 10^{-3})^2$$
$$1.8 \times 10^{-5}\ y - 1.8 \times 10^{-8} = 1.0 \times 10^{-6}$$
$$1.8 \times 10^{-5}\ y = 1.018 \times 10^{-6}$$
$$y \approx 0.057\ M \approx [HC_2H_3O_2]_0$$

Notice, the 5% rule approximation is not necessary in this Math, but you can still do it, if you want:

$$K_a = \frac{\left[C_2H_3O_2^-\right]\left[H_3O^+\right]}{\left[HC_2H_3O_2\right]}$$

$$1.8 \times 10^{-5} = \frac{\left(1.0 \times 10^{-3}\right)^2}{y - 1.0 \times 10^{-3}}$$

using the 5% rule approximation

$$1.8 \times 10^{-5} \approx \frac{\left(1.0 \times 10^{-3}\right)^2}{y}$$

$$\therefore \quad y \approx \frac{\left(1.0 \times 10^{-3}\right)^2}{1.8 \times 10^{-5}}$$

$$y \approx 0.056\ M \approx \left[HC_2H_3O_2\right]_0$$

The rounding difference is no big deal.

Solution 9: Calculate is the pH of a 0.20 M NaF solution? $K_a\,(\mathrm{HF}) = 7.2 \times 10^{-4}$

Remember, many salt solutions are not neutral. NaF is a salt of the weak acid HF, and is basic. Some people like to write the Brønsted proton transfer reaction like this:

$$NaF_{(aq)} + H_2O_{(l)} \rightleftharpoons Na^+_{(aq)} + HF_{(aq)} + OH^-_{(aq)}$$

I prefer to break the reaction down into two steps, because the Chemistry is clearer:

step 1: the 1-to-1 mole ratio salt dissociation:

$NaF_{(aq)}$	$\longrightarrow$	$Na^+_{(aq)}$	+	$F^-_{(aq)}$
0.20 *M*	$\longrightarrow$	0.20 *M*	+	0.20 *M*

step 2: the base equilibrium:

ICE-box:

	$F^+_{(aq)}$	+	$H_2O_{(l)}$	$\rightleftharpoons$	$HF_{(aq)}$	+	$OH^-_{(aq)}$
I	0.20 M				0		0
C	− x				+ x		+ x
E	0.20 M − x				x		x

Find $K_b\,(\mathrm{F}^-)$:

$$\begin{aligned} K_a\ K_b &= K_w \\ \therefore \quad K_b &= \frac{K_w}{K_a} \\ K_b\,(\mathrm{F}^-) &= \frac{1\times10^{-14}}{7.2\times10^{-4}} \\ K_b\,(\mathrm{F}^-) &\approx 1.39\times10^{-11} \end{aligned}$$

Equilibrium expression:

$$\begin{aligned} K_b &= \frac{[\mathrm{HF}]\,[\mathrm{OH}^-]}{\left[\mathrm{F}^+\right]} \\ 1.39\times10^{-11} &= \frac{x^2}{0.20-x} \end{aligned}$$

using the 5% rule approximation

$$\begin{aligned} 1.39\times10^{-11} &\approx \frac{x^2}{0.20} \\ 2.78\times10^{-12} &\approx x^2 \\ \therefore \quad x &\approx \sqrt{2.78\times10^{-12}} \\ x &\approx 1.67\times10^{-6}\ M = [\mathrm{OH}^-] \end{aligned}$$

Just like any other base, compute pOH and convert to pH:

$$\begin{aligned} \mathrm{pOH} &= -\log\,[\mathrm{OH}^-] \\ \mathrm{pOH} &= -\log\left[1.67\times10^{-6}\right] \\ &\approx -\left(-5.78\right) \\ \mathrm{pOH} &\approx 5.78 \end{aligned}$$

$$\begin{aligned} \mathrm{pH} + \mathrm{pOH} &= 14 \\ \therefore \quad \mathrm{pH} &= 14 - \mathrm{pOH} \\ &\approx 14 - 5.78 \\ \mathrm{pH} &\approx 8.22 \end{aligned}$$

Chapter 16: Buffers and solubility

Back in CHM 1100, we normally used one solute per solution. If we mixed two solutions, we wanted to react them.

It is possible to have two solutes coexisting in one solution. For example, mixing two ionic solutions does not always produce a precipitate, which is why we wrote NR, for "No Reaction." If the two solutes are unrelated, they don't affect each other. They can be treated almost as if they were two separate solutions.

However, multiple solutes may share the same cation or same anion – they have common ions. Common ions add their individual concentrations, increasing the effective concentration. Since these ions are products, Le Chatelier's Principle says common ions suppress the forward reaction of their solutes – they tend to cause a reverse equilibrium shift. This is called the COMMON ION EFFECT.

---

buffer solutions

An important common ion effect situation are buffer solutions.

What is a buffer solution?

A buffer solution has two specific solutes:

a weak acid plus a salt of that weak acid (the anion is its conjugate base)

OR a weak base plus a salt of that weak base (the cation is its conjugate acid).

Why is a buffer solution important?

A buffer has a stable pH. The pH stays very close to the original value even if some acid or base is added. The pH of most solutions is wildly unstable – adding a small amount of any acid or base will cause the pH to change a lot. Many reactions have equilibria that are sensitive to pH changes. If you need the reaction to run the way you expect, you should stabilize the pH with a buffer.

How does a buffer solution work?

The buffer's acid will neutralize any added base, and

the buffer's base will neutralize any added acid (up to the buffer capacity).

How do you choose a buffer pair?

$$\text{pH} \approx \text{p}K_a \quad \text{where} \quad \text{p}K_a = -\log K_a$$

Choose a conjugate pair with a pKa that is close to the protected pH.

What is the pH of a buffer solution?

use the Henderson-Hasselbach Equation:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[base]}{[acid]}\right)$$

Note: it perfectly possible to find the pH of a buffer using a common ion ICE-box equilibrium calculation, but it can become extremely complex. I don't recommend using the ICE-box.

---

acid-base titration

Titration was introduced in CHM 1100 Lab, where you slowly added one solution (in a buret) to another solution (in a flask), allowing the two chemicals to react, while making careful measurements.

In CHM 1200 Lab, the pH during an acid-base titration will be measured to draw the titration curve. In CHM 1200 Lecture, the pH at important points during an acid-base titration will be calculated.

An acid-base titration pH calculation has two parts. First is an acid-base neutralization stoichiometry problem. The results of the first part are transfer to the second part, which changes depending on where along the titration curve you are.

The two most important pH calculation points of an acid-base titration are inside the "buffer zone" and at the equivalence point. The equivalence point occurs when the moles of acid equal the moles of base – the neutralization is stoichiometrically complete. The equivalence point is the center of the nearly vertical part of the titration curve, and is pH = 7 for a strong acid and strong base titration, but not weak titration. The buffer zone is the nearly flat

---

solubility

In CHM 1100, we introduced "soluble" versus "insoluble" salts. Salts either dissolve or they don't, and we gave you YES/NO solubility rules.

soluble: $KCl_{(s)} \longrightarrow K^{+}_{(aq)} + Cl^{-}_{(aq)}$

insoluble: $AgCl_{(s)} \longrightarrow$ no reaction

This is incomplete. (In CHM 1100, we lied to you a lot, in order to keep things simple. In CHM 1200, we lie to you less.)

Insoluble salts are not completely insoluble. They are "sparingly" soluble. They will dissolve a small amount, and the salt exists in equilibrium with its ions.

sparingly soluble $AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$

with a heterogenous equilibrium expression called the solubility product:

$$K_{sp} = \left[Ag^{+}\right][Cl^{-}]$$

Be careful, many salts do not have 1-to-1 ion mole ratios – remember your ion charges.

If the number of ions is the same, the lower the K_{sp}, the lower the solubility, and vice versa.

The molar solubility of a sparingly soluble salt is found by solving the ICE-box equilibrium. The molar solubility is the saturation point. If any higher solubility is attempted, only the molar solubility will dissolve; the extra will precipitate. Notice, this is different concept of precipitation than in CHM 1100.

The common ion effect also applies to solubility and precipitation.

Note, so-called soluble salts are not infinitely soluble, either. There is a maximum amount; it's just large enough that we don't usually worry about it.

Chapter 16: Buffers and solubility Problems

Problem 1: (a) Calculate pH of a solution containing 0.25 M HF ($K_a = 7.2 \times 10^{-4}$) and 0.50 M NaF. (b) What would be the pH of the solution if 12.5 mL of 0.10 M HCl is added to 250 mL of the buffer?

Problem 2: A buffer solution of acetic acid ($K_a = 1.8 \times 10^{-5}$) and sodium acetate has a pH of 5.03. If the acetic acid concentration is 0.12 Molar, what is the concentration of the sodium acetate?

Problem 3: When 100.0 mL of 0.200 M HCI is titrated with 0.100 M NaOH, what is the pH after 100.0 mL of NaOH is added?

Problem 4: When 100.0 mL of 0.100 M $HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$ is titrated with 0.100 M NaOH, what is the pH after 50.0 mL of NaOH is added?

Problem 5: When 100.0 mL of 0.100 M $HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$ is titrated with 0.100 M NaOH, what is the pH after 100.0 mL of NaOH is added?

Problem 6: What is the molar solubility of strontium fluoride in pure water? $K_{sp}\,(SrF_2) = 7.9 \times 10^{-10}$.

Problem 7: What is the molar solubility of strontium fluoride in a 0.025 M NaF solution? $K_{sp}\,(SrF_2) = 7.9 \times 10^{-10}$.

Problem 8: The solubility of lithium carbonate is 7.4×10^{-2} mol/L. What is the solubility product constant of Li_2CO_3?

Problem 9: What mass of KF added to 500. mL of 0.030 M $Ba(NO_3)_2$ solution, will begin precipitation of solid BaF_2 ($K_{sp} = 2.4 \times 10^{-5}$)?

Problem 10: A 50.0-mL solution of 0.00200 M $AgNO_3$ is titrated with 50.0 mL of 0.00200 M $NaIO_3$. What mass of solid $AgIO_3$ would precipitate?

Chapter 16: Buffers and solubility Solutions

Solution 1: (a) Calculate pH of a solution containing 0.25 M HF ($K_a = 7.2 \times 10^{-4}$) and 0.50 M NaF. (b) What would be the pH of the solution if 12.5 mL of 0.10 M HCl is added to 250 mL of the buffer?

(a): weak acid is 0.25 M HF ($K_a = 7.2 \times 10^{-4}$)

conjugate base is F^-

$\mathbf{NaF}_{(aq)} \longrightarrow \mathbf{Na}^+_{(aq)} + \mathbf{F}^-_{(aq)}$
$0.50\ M \longrightarrow 0.50\ M + 0.50\ M$

$$\begin{aligned} pK_a &= -\log K_a \\ &= -\log\left(7.2 \times 10^{-4}\right) \\ pK_a &\approx 3.14 \end{aligned}$$

$$\begin{aligned} pH &= pK_a + \log\left(\frac{[base]}{[acid]}\right) \\ pH &\approx 3.14 + \log\left(\frac{[0.50\ M]}{[0.25\ M]}\right) \\ &\approx 3.14 + \log 2 \\ &\approx 3.14 + 0.30 \\ pH &\approx 3.44 \end{aligned}$$

Note: since I'm using the Henderson-Hasselbach Equation, I don't need the HF equilibrium reaction, nor its ICE-box.

(b) adding 12.5 mL of 0.10 M HCl strong acid to 250 mL buffer is a 262.5 mL dilution. Find diluted Molarities:

$$\begin{aligned} M_1\ V_1 &= M_2\ V_2 \\ \therefore \quad M_2 &= \frac{M_1\ V_1}{V_2} \\ &= \frac{0.10\ M\,\text{HCl}\left(12.5\ mL\right)}{262.5\ mL} \\ &\approx 0.0048\ M\,\text{HCl} \end{aligned}$$

$$
\begin{aligned}
M_1 \; V_1 &= M_2 \; V_2 \\
\therefore \quad M_2 &= \frac{M_1 \; V_1}{V_2} \\
&= \frac{0.25 \; M\,\text{HF}\,(250 \; mL)}{262.5 \; mL} \\
&\approx 0.2381 \; M\,\text{HF}
\end{aligned}
\qquad\qquad
\begin{aligned}
M_1 \; V_1 &= M_2 \; V_2 \\
\therefore \quad M_2 &= \frac{M_1 \; V_1}{V_2} \\
&= \frac{0.50 \; M\,\text{F}^-\,(250 \; mL)}{262.5 \; mL} \\
&\approx 0.4762 \; M\,\text{F}^-
\end{aligned}
$$

Note: since the HF and F^- Molarities change only slightly, it is not really necessary to calculate them.

pH calculation with diluted HF and F^- Molarities:

$$
\begin{aligned}
\text{pH} &= \text{p}K_a + \log\left(\frac{[base]}{[acid]}\right) \\
\text{pH} &\approx 3.14 + \log\left(\frac{0.4762 \; M - 0.0048 \; M}{0.2381 \; M + 0.0048 \; M}\right) \\
&\approx 3.14 + \log\left(\frac{0.4714 \; M}{0.2429 \; M}\right) \\
&\approx 3.14 + \log 1.941 \\
&\approx 3.14 + 0.288 \\
\text{pH} &\approx 3.43
\end{aligned}
$$

pH calculation with original HF and F^- Molarities:

$$
\begin{aligned}
\text{pH} &= \text{p}K_a + \log\left(\frac{[base]}{[acid]}\right) \\
\text{pH} &\approx 3.14 + \log\left(\frac{0.50 \; M - 0.0048 \; M}{0.25 \; M + 0.0048 \; M}\right) \\
&\approx 3.14 + \log\left(\frac{0.4952 \; M}{0.2548 \; M}\right) \\
&\approx 3.14 + \log 1.943 \\
&\approx 3.14 + 0.289 \\
\text{pH} &\approx 3.43
\end{aligned}
$$

See, they're the same answer, and very close to the original pH.

Solution 2: A buffer solution of acetic acid ($K_a = 1.8 \times 10^{-5}$) and sodium acetate has a pH of 5.03. If the acetic acid concentration is 0.12 Molar, what is the concentration of the sodium acetate?

The weak acid is 0.12 M $HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$ and the conjugate base is acetate $C_2H_3O_2^-$.

Remember: using the Henderson-Hasselbach Equation does not require the balanced equation, only knowing what the weak acid and conjugate base are.

$$\begin{aligned} \mathrm{p}K_a &= -\log K_a \\ &= -\log\left(1.8 \times 10^{-5}\right) \\ pK_a &\approx \color{red}{4.74} \end{aligned}$$

$$\begin{aligned} \mathrm{pH} &= \mathrm{p}K_a + \log\left(\frac{[base]}{[acid]}\right) \\ 5.03 &\approx 4.74 + \log\left(\frac{[C_2H_3O_2^-]}{0.12\ M}\right) \\ 0.29 &\approx \log\left(\frac{[C_2H_3O_2^-]}{0.12\ M}\right) \\ 10^{0.29} &\approx 10^{\log\left(\frac{[C_2H_3O_2^-]}{0.12\ M}\right)} \\ 1.950 &\approx \frac{[C_2H_3O_2^-]}{0.12\ M} \\ \therefore \quad [C_2H_3O_2^-] &\approx \color{red}{0.23\ M} \end{aligned}$$

Solution 3: When 100.0 mL of 0.200 M HCI is titrated with 0.100 M NaOH, what is the pH after 100.0 mL of NaOH is added?

Titrations are two-part problems. The first part is the neutralization stoichiometry. This can be done using the normal CHM 1100 stoichiometry technique:

step 1: convert givens to moles. Leaving in miliLiters and converting to millimoles saves a little time:

$$
\begin{aligned}
M &= \frac{mol}{L} \\
\therefore \quad mL \times M &= mmol \\
100.0\ mL \times 0.200\ M\ \text{HCl} &= mmol\ \text{HCl} \\
&= 20.0\ mmol\ \text{HCl} \\
100.0\ mL \times 0.100\ M\ \text{NaOH} &= mmol\ \text{HCl} \\
&= 10.0\ mmol\ \text{NaOH}
\end{aligned}
$$

step 2: the mole ratio can be done as a regular conversion, but I prefer a ICE-box-like method. Since neutralization is forward only, I call it the ICF-box – "F" for final.

	$\mathbf{HCl}_{(aq)}$ +	$\mathbf{NaOH}_{(aq)}$ ⟶	$\mathbf{NaCl}_{(aq)}$ +	$\mathbf{H_2O}_{(l)}$
I	20.0 mmol	10.0 mmol	0	
C	– 10.0 mmol	– 10.0 mmol	+ 10.0 mmol	
F	10.0 mmol	0	10.0 mmol	
	excess reagent	limiting reagent	neutral salt	

Notice: this is not just stoichiometry – its also limiting and excess reagent. In this case, the excess reagent is a strong acid. It will determine the pH. But, first complete the stoichiometry calculation.

step 3: convert excess from moles. Be careful to use the total volume of 200.0 mL:

$$
\begin{aligned}
M &= \frac{mol}{L} \\
&= \frac{10.0\ mmol}{200.0\ mL} \\
\text{excess}\ [\text{HCl}] &= 0.0500\ M
\end{aligned}
$$

Part 2 is to use the excess HCl to find the pH. This is straightforward, because HCl is a strong acid with 100% dissociation.

$\mathbf{HCl}_{(aq)}$	⟶	$\mathbf{H}^{+}_{(aq)}$	+	$\mathbf{Cl}^{-}_{(aq)}$
$0.0500\ M$	→	$0.0500\ M$	+	$0.0500\ M$

And use the pH formula:

$$
\begin{aligned}
\text{pH} &= -\log\left[\text{H}^{+}\right] \\
\text{pH} &= -\log\left[0.0500\right] \\
\text{pH} &\approx 1.30
\end{aligned}
$$

Solution 4: When 100.0 mL of 0.100 M $HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$ is titrated with 0.100 M NaOH, what is the pH after 50.0 mL of NaOH is added?

This problem is similar to the previous one, except that acetic acid is a weak acid, so the second part will be different.

Part 1 is stoichiometry.

step 1: convert givens to moles. Leave in miliLiters and convert to millimoles:

$$\begin{aligned} M &= \frac{mol}{L} \\ \therefore \quad mL \times M &= mmol \\ 100.0\ mL \times 0.100\ M\ \ HC_2H_3O_2 &= mmol\ \ HC_2H_3O_2 \\ &= 10.0\ mmol\ \ HCl \\ 50.0\ mL \times 0.100\ M\ \ NaOH &= mmol\ \ HCl \\ &= 5.00\ mmol\ \ NaOH \end{aligned}$$

step 2: I do the mole ratio with an ICF-box – “F” for final.

	$HC_2H_3O_2\,{}_{(aq)}$ +	**$NaOH_{(aq)}$** ⟶	**$NaC_2H_3O_2\,{}_{(aq)}$** +	**$H_2O_{(l)}$**
I	10.0 mmol	5.00 mmol	0	
C	– 5.00 mmol	– 5.00 mmol	+ 5.00 mmol	
F	5.00 mmol	0	5.00 mmol	
	excess reagent	limiting reagent	basic salt	

In this case, the excess reagent is a weak acid, and – more importantly – the product salt is its conjugate base. You’ve just made a buffer solution. It will determine the pH. But, first complete the stoichiometry calculation.

step 3: convert excess and product from moles back to Molarity. Use the 150.0mL total volume:

$$\begin{aligned} M &= \frac{mol}{L} \\ &= \frac{5.00\ mmol\ \text{excess}\ HC_2H_3O_2}{150.0\ mL} \\ \text{excess}\ \left[HC_2H_3O_2\right] &= 0.0500\ M \\ &= \frac{5.00\ mmol\ \text{product}\ C_2H_3O_2^{+}}{150.0\ mL} \\ \text{product}\ \left[C_2H_3O_2^{+}\right] &= 0.0500\ M \end{aligned}$$

Part 2: Again, this is a buffer solution. Whenever you do a "partial" titration of a weak acid or base with a strong base or acid, you will create a buffer – I call it the "buffer zone".

$$\begin{aligned} pK_a &= -\log K_a \\ &= -\log\left(1.8\times10^{-5}\right) \\ pK_a &\approx 4.74 \end{aligned}$$

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log\left(\frac{[base]}{[acid]}\right) \\ \text{pH} &\approx 4.74 + \log\left(\frac{0.0500\ M}{0.0500\ M}\right) \\ &\approx 4.74 + \log 1 \\ &\approx 4.74 + 0 \\ \text{pH} &\approx 4.74 \end{aligned}$$

Solution 5: When 100.0 mL of 0.100 M $HC_2H_3O_2$, $K_a = 1.8\times10^{-5}$ is titrated with 0.100 M NaOH, what is the pH after 100.0 mL of NaOH is added?

This problem is similar to the previous one, except that the NaOH volume is higher, so the second part will be different.

Part 1 is stoichiometry.

step 1: convert givens to moles. Leave in miliLiters and convert to millimoles:

$$\begin{aligned} M &= \frac{mol}{L} \\ \therefore\quad mL\times M &= mmol \\ 100.0\ mL\times0.100\ M\ \text{HC}_2\text{H}_3\text{O}_2 &= mmol\ \text{HC}_2\text{H}_3\text{O}_2 \\ &= 10.0\ mmol\ \text{HCl} \\ 100.0\ mL\times0.100\ M\ \text{NaOH} &= mmol\ \text{HCl} \\ &= 10.0\ mmol\ \text{NaOH} \end{aligned}$$

step 2: mole ratio using ICF-box.

	$HC_2H_3O_{2\,(aq)}$ +	$NaOH_{(aq)}$ ⟶	$NaC_2H_3O_{2\,(aq)}$ +	$H_2O_{(l)}$
I	10.0 mmol	10.0 mmol	0	
C	– 10.0 mmol	– 10.0 mmol	+ 10.0 mmol	
F	0	0	10.0 mmol	
			basic salt	

In this case, there is no limiting or excess reagent. The moles of the acid and base are equal – you're at the EQUIVALENCE POINT. Only the product, a basic salt, determines the pH.

Complete the stoichiometry calculation.

step 3: convert product from moles. The total volume is 200.0 mL:

$$\begin{aligned} M &= \frac{mol}{L} \\ &= \frac{10.0\ mmol\ \text{product}\ C_2H_3O_2^+}{200.0\ mL} \\ \text{product}\ \left[C_2H_3O_2^+\right] &= 0.0500\ M \end{aligned}$$

Part 2: Acetate is a Brønsted conjugate base. You need a real ICE-box.

	$\mathbf{C_2H_3O_2^+}_{(aq)}$	+ $\mathbf{H_2O}_{(l)}$ ⇌	$\mathbf{HC_2H_3O_2}_{(aq)}$ +	$\mathbf{OH^-}_{(aq)}$
I	0.0500 M		0	0
C	– x		+ x	+ x
E	0.0500 M – x		x	x

Find $K_b\left(C_2H_3O_2^+\right)$:

$$\begin{aligned} K_a\ K_b &= K_w \\ \therefore \quad K_b &= \frac{K_w}{K_a} \\ K_b\left(C_2H_3O_2^+\right) &= \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} \\ K_b\left(C_2H_3O_2^+\right) &\approx 5.56 \times 10^{-10} \end{aligned}$$

Equilibrium expression:

$$K_b = \frac{\left[HC_2H_3O_2\right]\,[OH^-]}{\left[C_2H_3O_2^-\right]}$$

$$5.56 \times 10^{-10} \approx \frac{x^2}{0.0500 - x}$$

using the 5% rule approximation

$$5.56 \times 10^{-10} \approx \frac{x^2}{0.0500}$$

$$2.78 \times 10^{-11} \approx x^2$$

$$\therefore \quad x \approx \sqrt{2.78 \times 10^{-11}}$$

$$x \approx \color{red}{5.27 \times 10^{-6}\ M = [OH^-]}$$

Just like any other base, find pOH and convert to pH:

$$\begin{aligned} pOH &= -\log\,[OH^-] \\ pOH &= -\log\left[5.27 \times 10^{-6}\right] \\ &\approx -\left(-5.28\right) \\ pOH &\approx \color{red}{5.28} \end{aligned}$$

$$\begin{aligned} pH + pOH &= 14 \\ \therefore \quad pH &= 14 - pOH \\ &\approx 14 - 5.28 \\ pH &\approx \color{red}{8.72} \end{aligned}$$

In my opinion, the equivalence point titration calculation of weak and strong is the longest calculation in CHM 1200, because it combines everything about acids and bases into one problem.

Solution 6: What is the molar solubility of strontium fluoride in pure water? $K_{sp}\,(SrF_2) = 7.9 \times 10^{-10}$.

K_{sp} problems are still equilibrium problems, so we still start with the ICE-Box:

	$\mathbf{SrF_2}_{\ (s)}$ ⇌	$\mathbf{Sr}^{2+}_{(aq)}$ +	$2\ \mathbf{F}^{-}_{(aq)}$
I		0	0
C		+ x	+ 2x
E		x	2x

Equilibrium expression:

$$
\begin{aligned}
K_{sp} &= \left[Sr^{2+}\right]\left[F^{-}\right]^{2} \\
7.9\times10^{-10} &= [x]\left[2x\right]^{2} \\
&= [x]\left[4x^{2}\right] \\
7.9\times10^{-10} &= 4x^{3} \\
1.975\times10^{-10} &= x^{3} \\
\therefore \quad x &= \sqrt[3]{1.975\times10^{-10}} \\
x &\approx 5.8\times10^{-4}\ M
\end{aligned}
$$

The molar solubility of strontium fluoride in pure water is $5.8\times10^{-4}\ mol/L$.

Notice, the ICE-box equilibrium calculation procedure has not changed.

Solution 7: What is the molar solubility of strontium fluoride in a 0.025 M NaF solution? $K_{sp}(SrF_2) = 7.9\times10^{-10}$.

This is a common ion effect problem – both salts are fluorides.

Sodium salts completely soluble:

$NaF_{(aq)}$	$\longrightarrow$	**$Na^{+}_{(aq)}$**	+	**$F^{-}_{(aq)}$**
$0.025\ M$	$\longrightarrow$	$0.025\ M$	+	$0.025\ M$

Transfer the fluoride ion to the strontium fluoride ICE-box:

	$SrF_{2\ (s)}$ $\rightleftharpoons$	**$Sr^{2+}_{(aq)}$** +	**$2\ F^{-}_{(aq)}$**
I		0	0.025 M
C		+ x	+ 2x
E		x	0.025 + 2x

Equilibrium expression:

$$K_{sp} = \left[\mathrm{Sr}^{2+}\right]\left[\mathrm{F}^-\right]^2$$

$$7.9 \times 10^{-10} = [x]\left[0.025 + 2x\right]^2$$

using the 5% rule approximation

$$\approx [x]\left[0.025\right]^2$$

$$7.9 \times 10^{-10} \approx 6.25 \times 10^{-4} x$$

$$\therefore \quad x \approx \frac{7.9 \times 10^{-10}}{6.25 \times 10^{-4}}$$

$$x \approx 1.3 \times 10^{-6}\ M$$

The molar solubility of strontium fluoride in 0.025 M NaF is $1.3 \times 10^{-6}\ mol/L$.

Notice, common ions always suppress solubility.

Solution 8: The solubility of lithium carbonate is 7.4×10^{-2} mol/L. What is the solubility product constant of Li_2CO_3?

Begin with the ICE-box. The trick is that "x" <u>is</u> the molar solubility:

	$\mathbf{Li_2CO_3}\ _{(s)}$ ⇌	$\mathbf{2\ Li^+_{(aq)}}$ +	$\mathbf{CO_3^-}\ _{(aq)}$
I		0	0
C		$+\,2(7.4 \times 10^{-2}\ M)$	$7.4 \times 10^{-2}\ M$
E		$1.48 \times 10^{-1}\ M$	$7.4 \times 10^{-2}\ M$

Equilibrium expression:

$$K_{sp} = \left[\mathrm{Li}^+\right]^2\left[\mathrm{CO}_3^{2-}\right]$$

$$= \left[1.48 \times 10^{-1}\right]^2\left[7.4 \times 10^{-2}\right]$$

$$\approx \left[2.19 \times 10^{-2}\right]\left[7.4 \times 10^{-2}\right]$$

$$K_{sp} \approx 1.6 \times 10^{-3}\ M$$

Solution 9: What mass of KF added to 500. mL of 0.030 M $Ba(NO_3)_2$ solution, will begin precipitation of solid BaF_2 ($K_{sp} = 2.4 \times 10^{-5}$)?

Be careful. Strictly speaking, the precipitation reaction (from CHM 1100) is:

$$Ba(NO_3)_{2\ (aq)} \ + \ 2\ KF_{(aq)} \ \longrightarrow \ BaF_{2\ (s)} \ + \ K_2NO_{3\ (aq)}$$

However, it is not important! You need to focus on the solubility of the BaF_2 precipitate. Begin by using the Ba^{2+} like a common ion. ICE-box:

	$\mathbf{BaF_{2\ (s)}}$ $\rightleftharpoons$	$\mathbf{Ba^{2+}_{(aq)}}$ +	$\mathbf{2\ F^-_{(aq)}}$
I		0.030 M	0
C		+ x	+ 2x
E		0.030 + x	2x

Equilibrium expression:

$$K_{sp} = \left[Ba^{2-}\right][F^-]^2$$

$$2.4 \times 10^{-5} = \left[0.030 + x\right]^2 \left[2x\right]$$

using the 5% rule approximation

$$2.4 \times 10^{-5} \approx \left[0.030\right]^2 \left[2x\right]$$

$$2.4 \times 10^{-5} \approx 1.8 \times 10^{-3}\ x$$

$$\therefore \quad x \approx 1.33 \times 10^{-2}\ M$$

$$[F^-] = 2x = 2\left(1.33 \times 10^{-2}\ M\right) = 2.66 \times 10^{-2}\ M$$

Since the fluoride ions come from KF, finish with stoichiometry for:

$$K^+_{(aq)} \quad + \quad F^-_{(aq)} \ \longrightarrow \ KF_{(s)}$$

You need the molar mass for KF – from way back in Chapter 3:

$$\begin{gathered}\text{KF}\\ \text{K} = 39.10\\ \text{F} = 19.00\\ \text{KF} = 58.10\ g/mol\end{gathered}$$

Remember, the problem gave a volume of 500. mL = 0.500 L:

$$0.500\ L \times \frac{2.66\times10^{-2}\ mol\ \text{F}^-}{L} \times \frac{1\ mol\ \text{KF}}{1\ mol\ \text{F}^-} \times \frac{58.10\ g\ \text{KF}}{1\ mol\ \text{KF}} \approx 0.77\ g\ \text{KF}$$

Notice, this is a perfectly normal 3-step stoichiometry calculation. There is no need for an ICF-box.

Solution 10: A 50.0-mL solution of 0.00200 M $AgNO_3$ is titrated with 50.0 mL of 0.00200 M $NaIO_3$. What mass of $AgIO_3$ would precipitate? (K_{sp} for $AgIO_3$ is 3.2×10^{-8}.)

The precipitation reaction is:

$$\text{AgNO}_{3\,(aq)} + \text{NaIO}_{3\,(aq)} \longrightarrow \text{AgIO}_{3\,(s)} + \text{NaNO}_{3\,(aq)}$$

In CHM 1100, we would have said that all of the $AgIO_3$ product would precipitate, because it was "insoluble," but in CHM 1200, it is "sparingly soluble". So, this is a two part problem. We must find the total mass produced, as well as the mass dissolved at the saturation point, and compare them.

Part 1: Use stoichiometry to find the total mass for the precipitation reaction.

step 1: convert givens to moles. Leave in miliLiters and convert to millimoles:

$$\begin{aligned} M &= \frac{mol}{L}\\ \therefore\quad mL\times M &= mmol\\ 50.0\ mL\times0.00200\ M\ \text{AgNO}_3 &= mmol\ \text{HC}_2\text{H}_3\text{O}_2\\ &= 0.100\ mmol\ \text{AgNO}_3\\ 50.0\ mL\times0.00200\ M\ \text{NaIO}_3 &= mmol\ \text{HCl}\\ &= 0.100\ mmol\ \text{NaIO}_3\end{aligned}$$

step 2: mole ratio using ICF-box.

	$AgNO_{3\,(aq)}$ +	$NaIO_{3\,(aq)}$ $\longrightarrow$	$AgIO_{3\,(s)}$ +	$NaNO_{3\,(aq)}$
I	0.100 mmol	0.100 mmol	0	
C	– 0.100 mmol	– 0.100 mmol	+ 0.100 mmol	+ 0.100 mmol
F	0	0	0.100 mmol	0.100 mmol
			precipitate	

The $AgIO_3$ is the possible precipitate, so find its total mass produced, by completing the stoichiometry calculation.

step 3: convert product from millimoles to grams. You need the molar mass for $AgIO_3$:

$$\begin{array}{rcl} & AgIO_3 & \\ Ag & & = 107.9 \\ I & & = 126.9 \\ O_3 = 16.00 \times 3 & & = \ 48.00 \\ & AgIO_3 \approx 282.8\ g/mol & \end{array}$$

$$0.100\ mmol\ AgIO_3 \times \frac{10^{-3}\ mol}{1\ mmol} \times \frac{282.8\ g\ AgIO_3}{1\ mol\ AgIO_3} \approx 0.0283\ g\ AgIO_3$$

Note: it is perfectly OK to do this as a perfectly normal 3-step stoichiometry calculation, but I think the ICF-box is a little faster when limiting/excess reagents are possible.

$$0.0500\ L \times \frac{0.00200\ mol\ AgNO_3}{L} \times \frac{1\ mol\ AgIO_3}{1\ mol\ AgNO_3} \times \frac{282.8\ g\ AgIO_3}{1\ mol\ AgIO_3} \approx 0.0283\ g\ AgIO_3$$

$$0.0500\ L \times \frac{0.00200\ mol\ NaIO_3}{L} \times \frac{1\ mol\ AgIO_3}{1\ mol\ NaIO_3} \times \frac{282.8\ g\ AgIO_3}{1\ mol\ AgIO_3} \approx 0.0283\ g\ AgIO_3$$

Part 2: Now, find the grams solubility, for the dissolved amount (saturation point). ICE-box:

	$AgIO_{3\ (s)}$ ⇌	**$Ag^+_{(aq)}$** +	**$IO^-_{3\ (aq)}$**
I		0	0
C		+ x	+ x
E		x	x

Equilibrium expression:

$$\begin{aligned} K_{sp} &= \left[Ag^+\right]\left[IO_3^-\right] \\ 3.2\times10^{-8} &= [x]\,[x] \\ 3.2\times10^{-8} &= x^2 \\ \therefore\quad x &\approx \sqrt{3.2\times10^{-8}} \\ x &\approx 1.79\times10^{-4}\ M \end{aligned}$$

Remember, "x" is the molar solubility. Convert to grams. (Total volume is 100.0 mL = 0.1000 L.)

$$0.1000\ \cancel{L}\times\frac{1.79\times10^{-4}\ mol\ \cancel{AgIO_3}}{\cancel{L}}\times\frac{282.8\ g\ AgIO_3}{1\ mol\ \cancel{AgIO_3}}\approx 0.0051\ g\ AgIO_3$$

Subtract for precipitate amount:

$$\begin{aligned} \text{precipitate} &= \text{total (stoichiometry)} - \text{dissolved (solubility)} \\ &\approx 0.0283\ g - 0.0051\ g \\ &\approx 0.0232\ g\ AgIO_3\ \text{precipitiate} \end{aligned}$$

Chapter 17: Thermodynamics

This chapter is a continuation of Chapter 5 (Thermochemistry). Chapter 5 discusses mostly enthalpy, ΔH°, which can be called the total energy.

There are other energy measurements besides enthalpy.

Free energy, ΔG°, is the energy "available to do work." Entropy, ΔS°, is a measurement of "waste" energy. Be careful: "work" and "energy" are ordinary English words. Regular people use them in regular conversation. That has absolutely nothing to do with what they mean in Chemistry. Do not mix up English and Chemistry. Remember, conservation of energy says energy can neither be created nor destroyed, only transformed from one kind into another, or transferred from one place or thing to another. When work is done, the work is the transform or transfer of energy.

When a chemical reaction (with an enthalpy) is used to run an engine (for example, burning gasoline to run a car), that engine cannot transform or transfer energy with 100% efficiency, not even in theory. Free energy and entropy compares the useful versus the waste energy out of the total.

Note: this topic is borrowed from Physics. On a problem solving level, there's less emphasis on Chemical reactions. Among other things, this means we're giving you the balanced equation again. You don't have to figure it out. But, it also means there are a lot of Mathematical formulae.

For example, the relationship between enthalpy, free energy and entropy is:

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$$

In addition, the products-subtract-reactants formation enthalpy formula also applies to free energy and entropy:

$$\begin{aligned}\text{From CHM 1100: } \Delta H^\circ_{rxn} &= \sum n_p\ \Delta H^\circ_f\ \text{(products)} - \sum n_p\ \Delta H^\circ_f\ \text{(reactants)}\\ \text{Now also: } \Delta G^\circ_{rxn} &= \sum n_p\ \Delta G^\circ_f\ \text{(products)} - \sum n_p\ \Delta G^\circ_f\ \text{(reactants)}\\ \text{and } S^\circ_{rxn} &= \sum n_p\ S^\circ\ \text{(products)} - \sum n_p\ S^\circ\ \text{(reactants)}\end{aligned}$$

Just like in CHM 1100, standard free energy and entropy are given to you on tables.

The free energy is most important in Chemistry, because it links to reaction "spontaneity". Does the reaction tend to proceed forward from reactants to products?

If ΔG° is negative, the reaction is SPONTANEOUS (it tends forward, to the right, to product side to equilibrium).

If ΔG° positive, the reaction is NONSPONTANEOUS (its tends reverse, to the left, to reactant side to equilibrium)

If $\Delta G^{\circ} = 0$, the reaction is AT EQUILIBRIUM and does not appear to shift either way.

Since we're talking about forward and reverse reactions, free energy is also directly related to equilibrium.

$$\Delta G^{\circ} = -RT \ln K$$

You should have noticed by now, everything in CHM 1200 leads back to equilibrium.

There is one very important twist: ΔG° versus ΔG – standard free energy vs. actual free energy (notice: with a degree symbol vs. no degree symbol). There is a difference between the free energy measured at standard conditions (per mole solids and liquids at 1 atm external pressure, at 1 atm partial pressures for gases and at 1 M for solutions) vs. your actual conditions (used in reaction quotient, Q)

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

Chapter 17: Thermodynamics Problems

Problem 1: For this reaction:

$$Fe_2O_{3\ (s)} + 3\ H_{2\ (g)} \longrightarrow 2\ Fe_{(s)} + 3\ H_2O_{(g)}$$

use the following data:

$$\Delta G_f^{\circ}\left[Fe_2O_{3\ (s)}\right] = -\ 743.5.\ kJ/mol,\ \Delta G_f^{\circ}\left[H_2O_{(g)}\right] = -\ 228.6\ kJ/mol$$

to determine if the reaction is spontaneous, and its equilibrium constant at 25 °C.

Problem 2: For the reaction, at 800. K:

$$N_{2\ (g)} + 3\ F_{2\ (g)} \rightleftharpoons 2\ NF_{3\ (g)}$$

the equilibrium partial pressures are measured as:

$$P_{N_2} = 0.021\ atm,\ P_{F_2} = 0.063\ atm,\ P_{NF_3} = 0.48\ atm$$

Calculate ΔG° for the reaction.

Problem 3: What is the equilibrium constant for this reaction at 1000 °C

$$CaCO_{3\ (s)} \rightleftharpoons CaO_{aq)} + CO_{2\ (g)}$$

Using the following data:

substance	ΔH_f°	S°
$CaCO_{3\ (s)}$	–1206.9 kJ/mol	92.9 J/mol · K
$CaO_{(s)}$	–635.1 kJ/mol	38.2 J/mol · K
$CO_{2\ (g)}$	–393.5 kJ/mol	213.7 J/mol · K

Problem 4: Calculate ΔG for the reaction:

$$HF_{(aq)} \rightleftharpoons H^+_{aq)} + F^-_{(aq)} \qquad K = 7.2 \times 10^{-4}$$

under the following conditions at 25 °C.

$$[HF] = 1.08\ M,\ \left[H^+\right] = [F^-] = 2.7 \times 10^{-3}\ M$$

Problem 5: At 298 K, the reaction:

$$N_2O_{4\,(g)} \rightleftharpoons 2\ NO_{2\,(g)}$$

has ΔH° and ΔS° values of +58.03 kJ and +176.6 J/K, respectively. What is the value of ΔG° at 298 K? Assuming that ΔH° and ΔS° do not depend on temperature, at what temperature does the reaction become spontaneous?

Chapter 17: Thermodynamics Solutions

Solution 1: For this reaction:

$$Fe_2O_{3\,(s)} \ + \ 3\ H_{2\,(g)} \ \rightleftharpoons \ 2\ Fe_{(s)} \ + \ 3\ H_2O_{(g)}$$

use the following data:

$$\Delta G_f^\circ \left[Fe_2O_{3\,(s)}\right] = -\,743.5.\ kJ/mol,\ \Delta G_f^\circ \left[H_2O_{(g)}\right] = -\,228.6\ kJ/mol$$

to determine if the reaction is spontaneous, and its equilibrium constant at 25 °C.

This problem requires two steps: the equilibrium constant is related to the reaction free energy, but the reaction free energy needs to be found from the formation free energies first (remember, elemental free energy is zero):

$$\begin{aligned}
\Delta G_{rxn}^\circ &= \sum n_p\ \Delta G_f^\circ\ \text{(products)} \ - \ \sum n_r\ \Delta G_f^\circ\ \text{(reactants)} \\
\Delta G_{rxn}^\circ &= \left(2\ Fe_{(s)} \ + \ 3\ H_2O_{(g)}\right) \ - \ \left(Fe_2O_{3\,(s)} \ + \ 3\ H_{2\,(g)}\right) \\
&= \left(\cancel{2\,(0)} \ + \ 3\left(-228.6\right)\right) - \left(-743.5 + \cancel{3\,(0)}\right) \\
\Delta G_{rxn}^\circ &= +57.7\ kJ/mol \\
\Delta G_{rxn}^\circ &= +5.77 \times 10^4\ J/mol
\end{aligned}$$

Since ΔG° is positive, the reaction is NONSPONTANEOUS.

$$\begin{aligned}
\Delta G^\circ &= -\,RT\ \ln K \\
5.77 \times 10^4 &= -\,8.314\,(298)\ \ln K \\
5.77 \times 10^4 &\approx -\,2478 \ln K \\
-23.28 &\approx \ln K \\
\therefore \quad e^{\ln K} &\approx e^{-23.28} \\
K &\approx 7.8 \times 10^{-11}
\end{aligned}$$

Notice: the reaction free energy is calculated in kJ/mol, but must be converted to J/mol to find the equilibrium constant.

Solution 2: At 800. K, the reaction:

$$N_{2\,(g)} \ + \ 3\ F_{2\,(g)} \ \rightleftharpoons \ 2\ NF_{3\,(g)}$$

has equilibrium partial pressures of:

$$P_{N_2} = 0.021\ atm,\ P_{F_2} = 0.063\ atm,\ P_{NF_3} = 0.48\ atm$$

Calculate ΔG° for the reaction.

This is also a two step problem, but the Math is different:

$$K_p = \frac{{P_{NF_3}}^2}{P_{N_2}\ {P_{F_2}}^3} = \frac{0.48^2}{0.021\,(0.063)^3}$$

$$K_p \approx 4.39 \times 10^4$$

$$\begin{aligned} \Delta G^\circ &= -RT\ \ln K \\ &= -8.314\,(800)\ \ln 4.39 \times 10^4 \\ &\approx -8.314\,(800)\,(10.69) \\ \Delta G^\circ &\approx -7.1 \times 10^4\ J \\ \Delta G^\circ &\approx -71\ kJ \end{aligned}$$

Notice: the reaction equilibrium expression is the same as it always is.

Solution 3: What is the equilibrium constant for this reaction at 1000 °C

$$CaCO_{3\,(s)} \rightleftharpoons CaO_{aq)} + CO_{2\,(g)}$$

Using the following data:

substance	ΔH_f°	S°
$CaCO_{3\,(s)}$	–1206.9 kJ/mol	92.9 J/mol · K
$CaO_{(s)}$	–635.1 kJ/mol	38.2 J/mol · K
$CO_{2\,(g)}$	–393.5 kJ/mol	213.7 J/mol · K

This problem requires multiple steps: the equilibrium constant uses the reaction free energy, but the reaction free energy needs the reaction enthalpy and entropy:

$$\begin{aligned} \Delta H_{rxn}^\circ &= \sum n_p\ \Delta H_f^\circ\ \text{(products)} - \sum n_r\ \Delta H_f^\circ\ \text{(reactants)} \\ \Delta H_{rxn}^\circ &= \left(CaO_{(s)} + CO_{2\,(g)}\right) - \left(CaCO_{3\,(s)}\right) \\ &= \left(-635.1\ kJ/mol + \left(-393.5\ kJ/mol\right)\right) - \left(-1206.9\ kJ/mol\right) \\ \Delta H_{rxn}^\circ &= +178.3\ kJ/mol \end{aligned}$$

$$\Delta S^{\circ}_{rxn} = \sum n_p\ S^{\circ}\ \text{(products)}\ -\ \sum n_r\ S^{\circ}\ \text{(reactants)}$$
$$\Delta S^{\circ}_{rxn} = \left(\text{CaO}_{(s)}\ +\ \text{CO}_{2\ (g)}\right)\ -\ \left(\text{CaCO}_{3\ (s)}\right)$$
$$= \left(38.2\ J/mol \cdot K + 213.7\ J/mol \cdot K\right) - \left(92.9\ J/mol \cdot K\right)$$
$$\Delta S^{\circ}_{rxn} = +159.0\ J/mol \cdot K$$
$$\Delta S^{\circ}_{rxn} = +0.1590\ kJ/mol \cdot K$$

Notice: the difference in units from the table – enthalpy is in kiloJoules, entropy is in Joules.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$
$$\Delta G^{\circ} = +\ 178.3\ kJ/mol - 1273\ K\left(+0.1590\ kJ/mol \cdot K\right)$$
$$\Delta G^{\circ} \approx -24.1\ kJ/mol$$

$$\Delta G^{\circ} = -\ RT\ \ln K$$
$$-2.41 \times 10^4 = -\ 8.314\,(298)\ \ \ln K$$
$$-2.41 \times 10^4 \approx -\ 2478 \ln K$$
$$9.728 \approx \ln K$$
$$\therefore \quad e^{\ln K} \approx e^{9.728}$$
$$K \approx 1.7 \times 10^4$$

Notice: there are a lot of steps, but the individual steps are not hard.

Solution 4: Calculate ΔG for the reaction:

$$\text{HF}_{(aq)}\ \rightleftharpoons\ \text{H}^+_{(aq)}\ +\ \text{F}^-_{(aq)} \qquad K = 7.2 \times 10^{-4}$$

under the following conditions at 25 °C.

$$[\text{HF}] = 1.08\ M,\ \left[\text{H}^+\right] = [\text{F}^-] = 2.7 \times 10^{-3}\ M$$

First use the equilibrium constant to find the standard free energy:

$$\Delta G^{\circ} = -\ RT\ \ln K$$
$$= -\ 8.314\,(298)\ \ \ln 7.2 \times 10^{-4}$$
$$\approx -\ 8.314\,(298)\,(-7.24)$$
$$\Delta G^{\circ} \approx +1.79 \times 10^4\ J/mol$$

Since the concentrations are not 1 Molarity, the free energy is nonstandard. I always find Q separately.

$$Q = \frac{[H^+]\,[F^-]}{[HF]} = \frac{[0.0027]^3}{[1.08]}$$

$$Q = 6.75 \times 10^{-6}$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$
$$\Delta G = +\,1.79 \times 10^4 + 8.314\,(298) \ln\left(6.75 \times 10^{-6}\right)$$
$$= +\,1.79 \times 10^4 + 8.314\,(298)\,(11.91)$$
$$\Delta G = +\,1.79 \times 10^4 + \left(-2.95 \times 10^4\right)$$
$$\Delta G = -1.16 \times 10^4 \; J/mol$$
$$\Delta G = -11.6 \; kJ/mol$$

Solution 5: At 298 K, the reaction:

$$N_2O_{4\,(g)} \rightleftharpoons 2\ NO_{2\,(g)}$$

has ΔH° and ΔS° values of +58.03 kJ and +176.6 J/K, respectively. What is the value of ΔG° at 298 K? Assuming that ΔH° and ΔS° do not depend on temperature, at what temperature does the reaction become spontaneous?

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$$
$$\Delta G^\circ = +\,58{,}030\ J/mol - 298\ K\left(+176.6\ J/mol \cdot K\right)$$
$$\Delta G^\circ \approx +5400\ J/mol$$

Since the free energy is positive at 298 K, this reaction is nonspontaneous at 298 K. Heating reactions with positive enthalpy and entropy, will eventually change the free energy to negative, and the reaction will become spontaneous. Since zero is the border between positive and negative numbers, setting the free energy to zero is used to determine the transition temperature.

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$$
$$0 = \Delta H^\circ - T\,\Delta S^\circ$$
$$T\,\Delta S^\circ = \Delta H^\circ$$
$$\therefore \quad T = \frac{\Delta H^\circ}{\Delta S^\circ}$$
$$T = \frac{58{,}030\ J/mol}{176.6\ J/mol \cdot K}$$
$$T \approx 329\ K$$

Chapter 19: Electrochemistry

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galvanic cells

A galvanic (or voltaic) cell is commonly called an electric battery. A battery is a device that produces electrical energy by a chemical reaction. The only chemical reaction type that directly involves a transfer of electrons are redox reactions.

Review redox reactions – especially half-reactions. Also now learn how to balance simple redox reactions, by making sure the half-reactions have equal number of electrons.

The most important battery measurement (besides size) is voltage – called electric potential in this class – which is an indirect energy measurement. There is a table of Standard Reduction Potentials, listing the known voltage values of dozens of reduction half-reactions, in numerical order.

The simplest way to build a battery is to run a redox reaction between any two metals (with their ions). (There is a section on real batteries and their real reactions in your textbook, that you may want to read, but that you are not responsible for.)

Since a redox reaction has both a reduction and an oxidation half-reaction, but there is no standard oxidation potential table, the rule is:

• the LOWER POTENTIAL from the table is the half-reaction that reverses to OXIDATION and is the ANODE half-cell, while

• the HIGHER POTENTIAL from the table is the half-reaction that stays as REDUCTION and is the CATHODE half-cell.

This will give a spontaneous cell – one that actually works as a battery and has a positive cell potential.

The standard cell potential is:

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

or if you also reverse the anode potential to get the oxidation potential:

$$E^{\circ}_{cell} = E^{\circ}_{red} + E^{\circ}_{ox}$$

Remember, when you are balancing electrons in half-reactions, you must multiply the half-reactions (in a Hess' Law-like procedure), but you must not multiply the voltage, because voltage is not measured per mole – it is an intensive property. Notice, we write the balanced equations with a single arrow. We're not too worried about equilibrium behavior – we want to reaction to go to completion.

In a cell diagram or cell notation, the anode/oxidation electrode is on the left and the cathode/reduction electrode is on the right. A salt bridge completes the circuit between the halves, by carrying additional ions against the electron flow to keep the charges neutral.

I said above that voltage is an indirect energy measurement. The direct energy value is the free energy:

$$\Delta G^{\circ} = -nFE^{\circ}$$

where n is the number of electrons in the balanced equation and F is the Faraday constant (electric charge per mole): $1\ mole\ e^{-} = 96{,}500\ Coulombs$. Remember, electrons are not visible in the complete balanced equation of a redox reaction – look at the half-reactions.

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the Nernst Equation

One very important twist: E° versus E – standard potential vs. actual potential (with a degree symbol vs. no degree symbol). Just like free energy, there is a difference between the potential measured at standard conditions (per mole solids and liquids at 1 atm external pressure, at 1 atm partial pressures for gases and at 1 M for solutions) vs. your actual conditions (used in reaction quotient, Q).

The Nernst Equation:

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

Since the temperature is almost always 298 K, R and F are constants, and there is a conversion factor between common and natural logs, the Nernst Equation can be rewritten:

$$E = E^{\circ} - \frac{0.0591}{n} \log Q$$

electrolytic cells

An electrolytic cell is the opposite of a galvanic cell. Galvanic cells have a positive cell potential and produce electrical energy in a spontaneous reaction. Electrolytic cells have a negative cell potential. Electricity is forced into electrolytic cells to run a nonspontaneous reaction. For example, this explains recharging a battery.

Electrolysis uses electrolytic cells to produce high purity metals from their ores. Electrolysis problems can be solved as stoichiometry problems. Remember these conversion factors:

Faraday constant (electric charge per mole): $1\ mole\ e^{-} = 96{,}500\ Coulombs$

electric current definition: $1\ Ampere = \frac{1\ Coulomb}{1\ s}$

Chapter 19: Electrochemistry Problems

Problem 1: A galvanic cell is built using the half-cells:

$$\begin{aligned} \mathrm{Au}^{3+} + 3\ e^- &\longrightarrow \mathrm{Au} \qquad E^\circ = 1.50\ Volts \\ \mathrm{Ag}^{+} + e^- &\longrightarrow \mathrm{Ag} \qquad E^\circ = 0.80\ Volts \end{aligned}$$

What are the overall cell reaction, the standard cell potential and the standard free energy?

Problem 2: A galvanic cell has the reaction:

$$3\ \mathrm{Mg}_{(s)} + 2\ \mathrm{Al}^{3+}_{(aq)} \longrightarrow 3\ \mathrm{Mg}^{2+}_{(aq)} + 2\ \mathrm{Al}_{(s)}$$

What are the cell's standard cell potential and standard free energy?

Problem 3: A galvanic cell has the notation:

$$\mathrm{Zn}\,|\,\mathrm{Zn}^{2+}\,(0.20\ M)\,||\,\mathrm{Fe}^{3+}\,(0.010\ M)\,|\,\mathrm{Fe}$$

What is the cell's potential?

Problem 4: What mass of Cu can be electrolyzed from aqueous Cu^{2+} solution, in 2.5 hours by an electric current of 25 Amperes?

Problem 5: How many hours will it take to produce 1.0 kg Cr from molten CrO_3 with a current of 100. A?

Chapter 19: Electrochemistry Solutions

Solution 1: A galvanic cell is built using the half-cells:

$$\begin{aligned} \mathrm{Au}^{3+} + 3\,e^- &\longrightarrow \mathrm{Au} \qquad E^\circ = 1.50\ Volts \\ \mathrm{Ag}^{+} + e^- &\longrightarrow \mathrm{Ag} \qquad E^\circ = 0.80\ Volts \end{aligned}$$

What are the overall cell reaction, the standard cell potential, the standard free energy and reaction equilibrium constant at 25 °C?

The silver's lower voltage indicates its half-reaction will reverse to oxidation as the anode. It also needs to be multiplied by 3 to balance the electrons (n = 3) with the gold half-reaction:

$$\begin{array}{lll} \text{red} & \mathrm{Au}^{3+} + 3\,e^- \longrightarrow \mathrm{Au} & E^\circ_{cath} = 1.50\ V \\ \text{ox} & 3\left(\mathrm{Ag} \longrightarrow \mathrm{Ag}^+ + e^-\right) & E^\circ_{an} = 0.80\ V \\ \text{overall} & 3\ \mathrm{Ag}_{(s)} + \mathrm{Au}^{3+}_{(aq)} \longrightarrow 3\ \mathrm{Ag}^+_{(aq)} + \mathrm{Au}_{(s)} & E^\circ_{cell} \end{array}$$

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= 1.50\ V - 0.80\ V \\ E^\circ_{cell} &= 0.70\ V \end{aligned}$$

Some people like to reverse the silver's voltage too, to get the oxidation voltage:

$$\begin{array}{lll} \text{red} & \mathrm{Au}^{3+} + 3\,e^- \longrightarrow \mathrm{Au} & E^\circ_{red} = \ \ 1.50\ V \\ \text{ox} & 3\left(\mathrm{Ag} \longrightarrow \mathrm{Ag}^+ + e^-\right) & E^\circ_{ox} = -0.80\ V \\ \text{overall} & 3\ \mathrm{Ag}_{(s)} + \mathrm{Au}^{3+}_{(aq)} \longrightarrow 3\ \mathrm{Ag}^+_{(aq)} + \mathrm{Au}_{(s)} & E^\circ_{cell} \end{array}$$

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{red} + E^\circ_{ox} \\ &= 1.50\ V + (-0.80\ V) \\ E^\circ_{cell} &= 0.70\ V \end{aligned}$$

Finding the free energy is simple, because it has a simple formula:

$$\begin{aligned}\Delta G^\circ &= -\,nFE^\circ \\ &= -\,2\left(96{,}500\right)(0.70) \\ &\approx -1.35\times 10^5\ J \\ \Delta G^\circ &\approx -135\ kJ\end{aligned}$$

Finding the equilibrium constant is also straightforward, because you can use the formula from Chapter 17 (remember to use Kelvins, not Celsius; and Joules, not kiloJoules):

$$\begin{aligned}\Delta G^\circ &= -\,RT\ln K \\ -1.35\times 10^5 &= -\,8.314\,(298)\ln K \\ -1.35\times 10^5 &\approx -\,2478\ln K \\ 54.49 &\approx \ln K \\ \therefore\quad e^{\ln K} &\approx e^{54.49} \\ K &\approx 4.6\times 10^{23}\end{aligned}$$

Solution 2: A galvanic cell has the reaction:

$$3\ \mathrm{Mg}_{(s)}\ +\ 2\ \mathrm{Al}^{3+}_{(aq)}\ \longrightarrow\ 3\ \mathrm{Mg}^{2+}_{(aq)}\ +\ 2\ \mathrm{Al}_{(s)}$$

What are the cell's standard potential and standard free energy?

Checking the Standard Reduction Potentials table for magnesium and aluminum, you will find:

$$\begin{aligned}\mathrm{Mg}^{2+}\ +\ 2\ e^-\longrightarrow\ \mathrm{Mg}\qquad & E^\circ = -\,2.37\ V \\ \mathrm{Al}^{3+}\ +\ 3\ e^-\longrightarrow\ \mathrm{Al}\qquad & E^\circ = -\,1.66\ V\end{aligned}$$

However, the magnesium is backwards when compared with the balanced equation, and needs to be reversed to oxidation (anode):

$$\begin{aligned}\text{ox}\qquad \mathrm{Mg}\ \longrightarrow\ \mathrm{Mg}^{2+}\ +\ 2\ e^-\qquad & E^\circ_{an} = -\,2.37\ V \\ \text{red}\qquad \mathrm{Al}^{3+}\ +\ 3\ e^-\ \longrightarrow\ \mathrm{Al}\qquad & E^\circ_{cath} = -\,1.66\ V\end{aligned}$$

The half-reactions also need to be multiplied to be balanced at 6 electrons (n = 6):

$$\begin{array}{lll} \text{ox} & 3\left(\text{Mg} \longrightarrow \text{Mg}^{2+} + 2\ e^-\right) & E^\circ_{an} = -\,2.37\ V \\ \text{red} & 2\left(\text{Al}^{3+} + 3\ e^- \longrightarrow \text{Al}\right) & E^\circ_{cath} = -\,1.66\ V \end{array}$$

Now use your formulae:

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= -\,1.66\ V - (-2.37)\ V \\ E^\circ_{cell} &= 0.71\ V \end{aligned}$$

$$\begin{aligned} \Delta G^\circ &= -\,nFE^\circ \\ &= -\,6\left(96{,}500\right)(0.71) \\ &\approx -4.11 \times 10^5\ J \\ \Delta G^\circ &\approx -411\ kJ \end{aligned}$$

Solution 3: A galvanic cell has the notation:

$$\text{Zn}\,|\,\text{Zn}^{2+}\,(0.20\ M)\,||\,\text{Fe}^{3+}\,(0.010\ M)\,|\,\text{Fe}$$

What is the cell's potential?

Checking the Standard Reduction Potentials table for zinc and iron, you will find:

$$\begin{array}{ll} \text{Zn}^{2+} + 2\ e^- \longrightarrow \text{Zn} & E^\circ = -\,0.76\ Volts \\ \text{Fe}^{3+} + 3\ e^- \longrightarrow \text{Fe} & E^\circ = -\,0.04\ Volts \end{array}$$

However, a cell notation writes the oxidation/anode on the left, so the zinc is needs to be reversed:

$$\begin{array}{lll} \text{ox} & \text{Zn} \longrightarrow \text{Zn}^{2+} + 2\ e^- & E^\circ_{an} = -\,0.76\ V \\ \text{red} & \text{Fe}^{3+} + 3\ e^- \longrightarrow \text{Fe} & E^\circ_{cath} = -\,0.04\ V \end{array}$$

The half-reactions also need to be multiplied to be balanced at 6 electrons (n = 6) for the overall cell reaction:

$$\begin{array}{lll} \text{ox} & 3\left(\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\ e^-\right) & E^\circ_{an} = -\,0.76\ V \\ \text{red} & 2\left(\text{Fe}^{3+} + 3\ e^- \longrightarrow \text{Fe}\right) & E^\circ_{cath} = -\,0.04\ V \\ \text{overall} & 3\ \text{Zn}_{(s)} + 2\ \text{Fe}^{3+}_{(aq)} \longrightarrow 3\ \text{Zn}^{2+}_{(aq)} + \text{Fe}_{(s)} & E^\circ_{cell} \end{array}$$

You can now find the standard cell potential:

$$\begin{aligned} E^{\circ}_{cell} &= E^{\circ}_{cathode} \ - \ E^{\circ}_{anode} \\ &= -\,0.04\ V - \left(-0.76\right)\ V \\ E^{\circ}_{cell} &= 0.72\ V \end{aligned}$$

The Molarities are non-standard, so you need to use the actual conditions in the original question to find the actual potential. I always find Q separately, before using the Nernst Equation:

$$\begin{aligned} Q &= \frac{\left[\mathrm{Zn}^{2+}\right]^3}{\left[\mathrm{Fe}^{3+}\right]^2} \\ &= \frac{\left[0.20\right]^3}{\left[0.010\right]^2} \\ Q &= 80 \end{aligned}$$

$$\begin{aligned} E &= E^{\circ} - \frac{0.0591}{n} \log Q \\ E &= 0.72 - \frac{0.0591}{6} \log 80 \\ E &\approx 0.72 - 0.00985\,(1.90) \\ E &\approx 0.72 - 0.02 \\ E &\approx 0.70\ V \end{aligned}$$

Solution 4: What mass of Cu can be electrolyzed from aqueous Cu^{2+} solution, in 2.5 hours by an electric current of 25 Amperes?

The reduction half-reaction from the Standard Reduction Potentials table is:

$$\mathrm{Cu}^{2+} \ + \ 2\ e^- \ \longrightarrow \ \mathrm{Cu} \qquad E^{\circ}_{red} = 0.43\ V$$

Remember, electrolysis is a stoichiometry problem. We don't need the voltage.

step 1: convert given current to moles – start with the time and use current definition and Faraday constant
step 2: convert given to unknown – use mole ratio
step 3: convert unknown from moles – use molar mass

$$2.5\ hr \times \frac{3600\ s}{1\ hr} \times \frac{25\ Coulombs}{1\ s} \times \frac{1\ mol\ e^-}{96{,}500\ Coulombs} \times \frac{1\ mol\ \mathrm{Cu}}{2\ mol\ e^-} \times \frac{63.55\ g\ \mathrm{Cu}}{1\ mol\ \mathrm{Cu}} \approx 74\ g\ \mathrm{Cu}$$

Solution 5: How many hours will it take to produce 1.0 kg Cr from molten CrO_3 with a current of 100. A?

CrO_3 is not on the Standard Reduction Potentials table, but that's OK – we don't need the voltage. You should be able to determine the balanced half-reaction:

$$\mathrm{Cr}^{6+} \; + \; 6 \; e^{-} \; \longrightarrow \; \mathrm{Cr}$$

Otherwise, this is the opposite of the previous electrolysis stoichiometry (1.0 kg = 1000 g):

$$1000 \; g \;\; \mathrm{Cr} \times \frac{1 \; mol \; \mathrm{Cr}}{52.00 \; g \;\; \mathrm{Cr}} \times \frac{6 \; mol \; e^{-}}{1 \; mol \; \mathrm{Cr}} \times \frac{96{,}500 \; Coulombs}{1 \; mol \; e^{-}} \times \frac{1 \; s}{100 \; Coulombs} \times \frac{1 \; hr}{3600 \; s} \approx 31 \; hr$$