

Welcome to CHE-NYB

- This course builds upon NYA: measurement (sig figs still count!), stoichiometry, limiting reagent, net ionic equation/spectator ions, solution (acid/base) chemistry, Ideal Gas Law, Lewis Structures/Resonance, Electronegativity/Atom Size, intermolecular forces.
- Essentially this course can be divided into the following subsections: Thermodynamics (ΔH , ΔE , Entropy and Free Energy), Equilibrium and Practical Examples of Equilibrium Processes with Solution Chemistry (includes Electrochemistry), and Kinetics

Lecture Concepts 1. Intro to Thermochemistry Chapter 6 Zumdahl Chemistry

Define **energy**. energy = capacity to do work or to produce heat

Thermodynamics = thermochemistry. = science of energy transformations

Why should you care about thermodynamics?

Harnessing matter to heat or cool an environment
or harnessing matter to do work (such as to power an engine)

Guiding Principle: First Law of Thermodynamics = Law of Conservation of Energy:

The total energy of the universe is constant = energy can be neither created nor destroyed, only transformed from one form to another.

The First Law of Thermodynamics should be in the forefront of your thinking as you do thermodynamics problems.

Dividing our thoughts into two types of energy:

1. Kinetic Energy (of a particle or object): = K.E. Define and write a mathematical equation.

SI unit of
energy = J = Joule
 $1J = 1\text{kg} \cdot \frac{\text{m}^2}{\text{s}^2}$

$$K.E. = \frac{1}{2}mv^2$$

m = mass of object / particle

v = velocity of object / particle

2. Potential Energy = Chemical Potential Energy = P.E.

P.E. = energy due to chemical composition

Define internal energy (E): sum of kinetic energy plus the potential energy of the system.

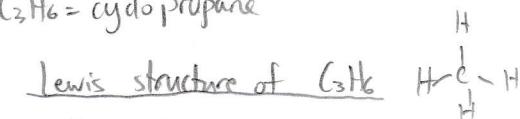
For today
 C_3H_8 = cyclopropane

Definitions:

Two types of energy transfer:

① q = heat

② w = work



c is sp^3 hybridized.

(Around an sp^3 hybridized atom, having bond angles of 109.5°)
 Due to the equilateral triangle of carbons, C-C-C bond angles must be 60°
 keeps in CH_4 , for example, the single bonds as far apart as possible)

While q is often associated with a change in temperature, give one example where it is not: heat in a phase change
 phase = state of matter

When you are doing a thermodynamics problem, you'll want to divide your thoughts into two parts:

System: The part of the universe one is focusing one's attention on

Surroundings: Everything outside the system

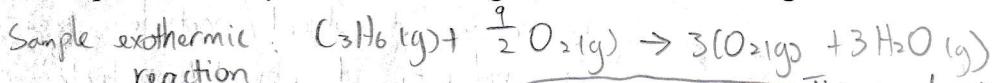
Depends on problems

What should you think of as system? If a reaction is occurring, one should think of the system as the relative internal energies of reactants and products. If one has unreactive substances, it's helpful to think of surroundings as the substances themselves.

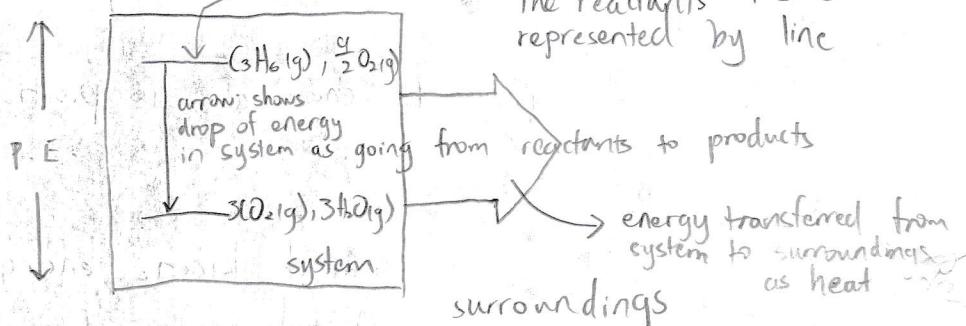
Surroundings would include the reaction flask, the solvent and the air above a flask assuming these are not a part of the reaction occurring. If a reaction is occurring, thinking Draw a potential energy diagram box for a sample exothermic reaction (examples of changes exothermic reactions: combustion of hydrocarbon, bond-forming or I.F.-forming in temperature process). I.F. = intermolecular force

surroundings all outside as surroundings is
 ↑ the box helpful.

What represents the system for this diagram? The surroundings?



moving up box,
 the P.E. increases



Define exothermic.

Exothermic Process = process where energy is transferred from system to surroundings as heat.

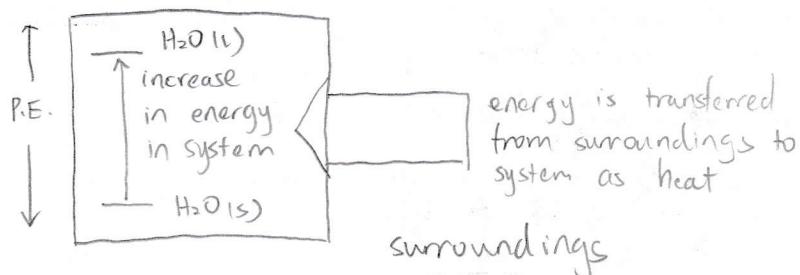
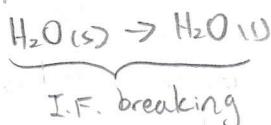
Endothermic process = process where energy is

Define endothermic. transferred from surroundings to system as heat

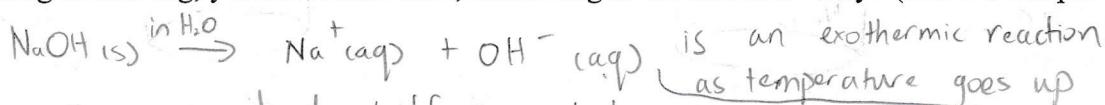
Draw a potential energy diagram box to show an endothermic process or reaction. (examples of endothermic reactions: bonds breaking, I.F.s breaking).

P.E. diagram box for an endothermic process

Sample
endothermic
process



Potential point of confusion: When ionic compounds dissolve, the dissolution may be endothermic or exothermic, depending on the ionic compound dissolving. An ionic bond is breaking during dissolving, yet for certain salts, dissolving is exothermic. Why? (Show a sample reaction.)



Yes, breaking the ionic bond itself is endothermic,
but the solvation of the ions is exothermic

(The solvation of ions = intermolecular forces forming when the
solvent surrounds the ions)

Assuming the heat released or absorbed in a reaction does not result in a phase change or the occurrence of another reaction, what happens to the temperature for an endothermic process? Exothermic process? Why?

For endothermic process: the temperature can only decrease

For exothermic process: the temperature can only increase

Why? The total energy of universe is constant.

State function = state property = property that is independent of

pathway = property that only depends on the present not
the past or future.

Energy and volume are state functions, but heat and work are not. Explain.

E and V depend only on the present.

e.g. 1 mol $\text{CO}_2(\text{g})$ has a certain energy and
volume at STP associated with it, it
doesn't matter how that mole of $\text{CO}_2(\text{g})$ was created

$$\Delta E = (\text{internal energy})_{\text{final}} - (\text{internal energy})_{\text{initial}}$$

Delta with thermodynamic functions means? $\Delta E = q + w$

$$\Delta(\text{something}) = (\text{something})_{\text{final}} - (\text{something})_{\text{initial}}$$

Four thermodynamic
functions (seen in
this course)

$\underbrace{\text{E}, \text{H}, \text{G}, \text{S}}$
we'll see these later

Equations you'll see later:

$$\text{heat} = m \cdot c \cdot \Delta T$$

$$\text{work} = -P \cdot \Delta V$$

* The delta present
in the equations
for heat & work
tell us that heat &
work are not
state functions

m = mass of substance X

c = specific heat capacity
of substance X

T = temperature

P = pressure

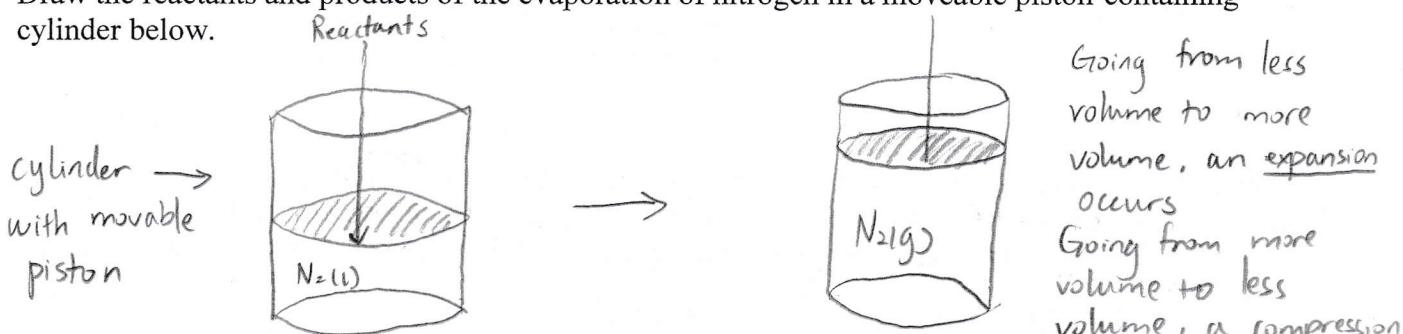
V = volume

For $\Delta E = q + w$ calculations, see the reaction always from the system's viewpoint.

Remember that energy = the capacity to do work or produce heat. If energy is transferred from system to the surroundings as heat during a reaction, the reaction is exothermic and sign of "q" is negative since the system has less capacity to produce heat after the exothermic reaction is complete. If energy is transferred from surroundings to system as heat the reaction is endothermic and the sign of "q" is positive since the system has more capacity to produce heat after the endothermic reaction is complete.

Consider the following process: $N_2(l) \rightarrow N_2(g)$...

Draw the reactants and products of the evaporation of nitrogen in a moveable piston-containing cylinder below.



When there are more gases on the product side of the equation than on the reactant side of the equation, an **expansion** is said to be done and the system does work on the surroundings. For an expansion, the sign of w is negative since once the system has expanded it has less capacity to do expansion work. When there are more gases on the reactant side of the equation than on the product side of the equation, a **compression** is said to be done, the surroundings do work on the system and the sign of w is said to be positive since the system has more capacity to do expansion work.

Units of energy: J, cal, Cal

$$\text{calorie} = \text{cal} = 4.18 \text{ J}$$

$$\text{food calorie} = \text{Cal} = 1000 \text{ cal} = 1 \text{ kcal}$$

Problem: Calculate ΔE for the following statements.

- An endothermic reaction involves absorbing of heat by system
- A system of gases absorbs 40 J of heat while 30 J of expansion work are performed by it.

$$\Delta E = +40 \text{ J} - 30 \text{ J} = +10 \text{ J}$$

- An exothermic reaction involves releasing of heat by system
- A system of gases releases 50J of heat and 40 J of compression work are done on it.

$$\Delta E = -50 \text{ J} + 40 \text{ J} = -10 \text{ J}$$

Lecture Concepts 2. Work calculations (expansion & compression of an ideal gas)

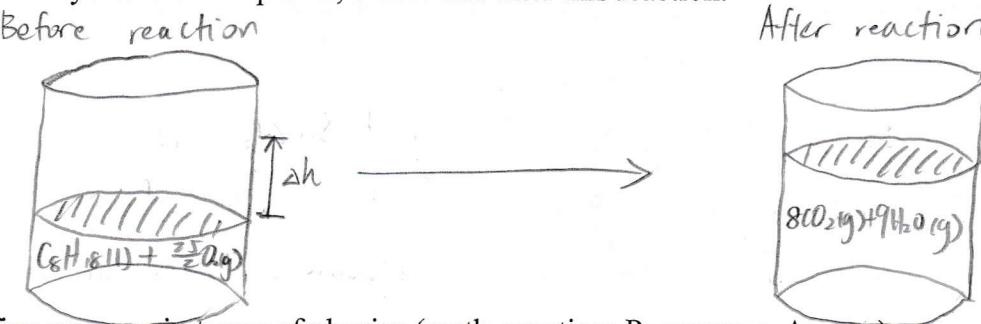
Consider the equation for the combustion of octane: $C_8H_{18} + \frac{25}{2}O_2 \rightarrow 8CO_2 + 9H_2O$



For the combustion of octane, if the gases were in a cylinder, would the result be an expansion, a pushing back of the piston by the gases or a compression?

Expansion occurs since there's more moles of gas on product side of the equation than on reactant side of the equation.

Draw a cylinder with a piston, before and after this reaction.



Define pressure in terms of physics (math equation; P=pressure, A=area):

$$P = \frac{\text{Force}}{A}$$

Define work in terms of physics (math equation):

$$\text{work} = (\text{Force}) \times (\text{distance})$$

What is the work in the context of an expansion or compression? (Δh = change in height= final height- initial height; ΔV = change in volume= final volume – initial volume)

$$\text{work} = (\text{Force}) \times (\Delta h)$$

Substitute $P \cdot A$ for Force in the above equation

$$\text{work} = (P \cdot A) \times \Delta h$$

What is $A \cdot \Delta h$? ΔV

This leads us to the common equation used for work problems...

For
expansion/compression : $w = -P \cdot \Delta V$

However, pay SPECIAL ATTENTION to the SIGN; we're seeing things from the point of view of the SYSTEM, remember. What would the sign be in an expansion (ΔV is positive)?

sign of work is negative in an expansion

$$w = -P\Delta V$$

- For a number of work problems, one will end up with units of L*atm as an answer.
- Joules are a more common unit to express energy... here's an easy way of remembering how to convert L*atm to Joules in case you forget...

L·atm is a unit of energy

$$R = 8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}} = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}$$

$$\frac{8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}} = \frac{101.3 \text{ J}}{1 \cdot \text{L} \cdot \text{atm}}$$

$$101.3 \text{ J} = 1 \text{ L} \cdot \text{atm}$$

Problem: Calculate work (w) when 50.0g of tin are dissolved in excess hydrochloric acid at 1.00 atm and 25°C. (For problems involving work with gases in this course, assume ideal gas behaviour.)

For this problem
an equation will
be provided.

limiting reagent



more moles of gas on product side of

equation, so therefore an expansion is occurring

P_{ex} = external pressure

$$w = -P \cdot \Delta V$$

$$w = -(1.00 \text{ atm}) \Delta V = -10.3 \text{ L} \cdot \text{atm}$$

$$\Delta V = \frac{R \cdot T \cdot \Delta n}{P} = \frac{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \cdot 298 \text{ K} \cdot 0.4214 \text{ mol}}{1.00 \text{ atm}} = 10.3 \text{ L}$$

$$\Delta n = (\text{moles of gas})_f - (\text{moles of gas})_i$$

$$\Delta n = 50.0 \text{ g Sn} \times \frac{\text{mol Sn}}{118.7 \text{ g Sn}} \times \frac{\text{mol H}_2}{\text{mol Sn}} = 0.4212 \text{ mol H}_2$$

$$[-10.3 \text{ L} \cdot \text{atm}]$$

Work of expansion and compression of gases is described sometimes as PV work. For the time being, PV work is the only type of work you need to concern yourself with. So, think that the only reactions where you need to concern yourself with work is where the moles of gas are different on the product side of the equation relative to the reactant side of the equation.

Thinking real world, why care about expansion or compression of gases?

Powering Engines

Lecture Concepts 3: Enthalpy and Calorimetry

2nd Define enthalpy (H):

thermodynamic function

$$\text{enthalpy} = H = E + PV$$

(of system)

E = internal energy (of system)

P = pressure

V = volume

Is enthalpy a state function? Yes, since E, P, V are state functions

subsets of q_p = heat absorbed or released under constant pressure conditions. Why is so much thermodynamic data at constant P? A lot of reactions are done in a lab at atmospheric pressure

What does q_v mean? heat absorbed or released under constant volume conditions

At constant pressure, derive an equation that relates ΔE and ΔH . Then, manipulate the equation to show how $q_p = \Delta H$. $\Delta H = \Delta E + P\Delta V$

at constant pressure $\Delta H = \Delta E + P\Delta V$

$$\Delta H = q_p + w + P\Delta V = q_p - P\Delta V + P\Delta V$$

$\Delta H = q_p$

At a given temperature, one might also express the relationship between ΔE and ΔH as follows (for the purposes of this course, ideal gas equation conditions are assumed). From Ideal Gas Law

At constant pressure

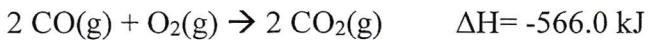
$$\Delta H = \Delta E + P\Delta V$$

$$\boxed{\Delta H = \Delta E + R \cdot T \cdot \Delta n}$$

at a certain temperature $\rightarrow P \cdot \Delta V = R \cdot T \cdot \Delta n$

$\Delta n = (\text{mol of gas})_f - (\text{mol of gas})_i$

Problem: Calculate the change in internal energy when 2 moles of carbon monoxide are converted to two moles of carbon dioxide at 1 atm pressure and 25°C.



$$\Delta E = \Delta H - R \cdot T \cdot \Delta n$$

$$= -566.0 \text{ kJ} - 0.008314 \frac{\text{kJ}}{\text{K} \cdot \text{mol}} (298 \text{ K}) (-1)$$

↑ ↑
energy units must be the same
in both parts of equation

$$\boxed{\Delta E = -563.5 \text{ kJ}}$$

↑
Note that the ΔE value
is very close to the ΔH
value (since work is much less than heat
occurs)

Panic-Prevention Note: You might panic, thinking, oh it's exothermic, so do I have to worry about the temperature going up??? DO NOT PANIC. For this equation, if given a temperature, assume that temperature is constant. (The reaction could be done in a water bath of such a size that any temperature change is negligible)

* So, at (key two words) constant pressure, the CHANGE in enthalpy is equal to the energy transfer as heat, so the change in enthalpy = heat of reaction at constant pressure.

The following five vocabulary terms for heats of reaction assume constant pressure conditions (if one has constant volume conditions, one must replace the ΔH for all these vocabulary terms with ΔE as we will see later).

1. $\Delta H_{rxn} = \Delta H$ = heat of reaction = change of enthalpy when a reaction occurs = *enthalpy of reaction*
2. $\Delta H_{sol'n}$ = heat of solution = change of enthalpy associated with a substance completely dissolving = *enthalpy of solution*
3. ΔH_{fus} = heat of fusion = change of enthalpy associated with a substance completely melting
4. ΔH_{vap} = heat of vaporization = change of enthalpy associated with a substance completely boiling
5. $\Delta H_{combustion}$ = heat of combustion = change of enthalpy as a combustion reaction occurs

So, ΔH is the q at constant pressure. Will there always be a change in temperature as a reaction occurs? *No, remember that a reaction can cause a change in a state of matter rather than a temperature change.*

If you see $\Delta H = 68 \text{ kJ}$ for $\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$, is this the ΔH for one molecule of nitrogen reacting with two molecules of oxygen converting to two molecules of NO_2 gas?

$\Delta H = 68 \text{ J}$ is the ΔH as one mole of $\text{N}_2(\text{g})$ reacts with 2 moles of $\text{O}_2(\text{g})$ completely to give 2 moles of $\text{NO}_2(\text{g})$

ΔH and other Δ thermodynamic functions (ΔE , ΔG , ΔS) are listed **per mole of reaction**.

A **mole of reaction** or "a mole of reaction as written" means that one multiplies all coefficients of reactants and products in a reaction by a mole that are shown in the chemical equation.

How does one determine ΔH (or ΔE) from experiment?

Define **calorimetry**. = *Science of measuring heat flow*

Define **calorimeter**. = *Device in which heat flow is measured*

Specific heat capacity = $c = s$. The energy required to raise 1 gram of substance 1 degree Celsius.

Molar heat capacity = $c_m = s_m$. The energy required to raise 1 mole of substance 1 degree Celsius.

Given your experience with life so far, would you expect the specific heat capacity to be greater for a wooden spoon or a metal spoon?

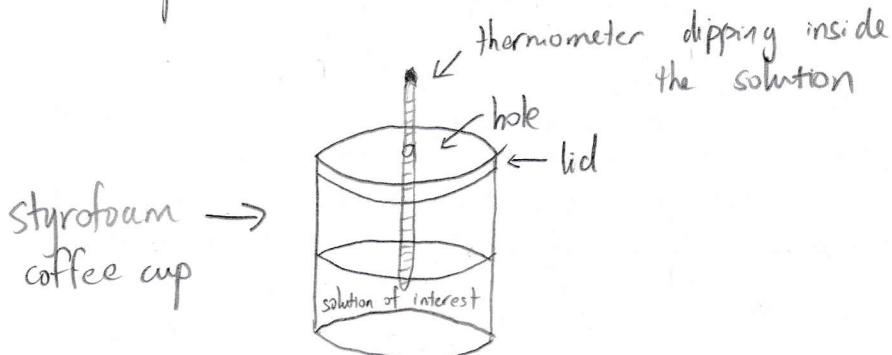
*wooden spoon has the greater specific heat capacity
(the metal spoon burns your hand quickly stirring hot soup)*

specific heat capacity = $C_{H_2O} = 4.18 \text{ J/g}\cdot\text{C} = 4.18 \text{ J/g}\cdot\text{K}$ ← Why? A change in units of C is the same as a change in units of K .

for H_2O
Why is the value for specific heat capacity (or molar heat capacity) the same for a given substance if written in units of $\text{J}/^\circ\text{C} \cdot \text{g}$ or $\text{J}/\text{K} \cdot \text{g}$ (or $\text{J}/^\circ\text{C} \cdot \text{mol}$ is the same as $\text{J}/\text{K} \cdot \text{mol}$)?

Draw a **constant-pressure calorimeter** which is also known as a:

coffee cup calorimeter



One coffee cup or two nested coffee cups in a constant-pressure calorimeter are typically made out of polystyrene (polystyrene= Styrofoam).

Q: Why might you imagine that this material is used to measure heat released or absorbed during chemical reactions? (Don't need to worry about what's outside the calorimeter for calorimetry problems...) *Styrofoam is an excellent insulator.*

Calorimeter constant = **calorimeter heat capacity** = C_{cal} . The energy required to raise a calorimeter 1 degree C.

- For calorimeter problems, if no calorimeter constant is given, you may assume that the heat absorbed or released by the calorimeter is negligible. However, **IF** the C_{cal} **IS** given or **IF**, in an experiment, you are given the opportunity to DETERMINE the C_{cal} experimentally, you **SHOULD** then use the calorimeter constant.

In a calorimeter, the heat absorbed or released by a substance that involves a change of temperature of that substance = $m \cdot c \cdot \Delta T$ or $n \cdot c_m \cdot \Delta T$ and the heat absorbed or released by the calorimeter containing the system = $C_{\text{cal}} \cdot \Delta T$ where m = mass of that substance, c =specific heat capacity of that substance; n = moles of that substance c_m =molar heat capacity of that substance and T =temperature. For our purposes (not exactly true, an approximation) in problems, imagine that the specific heat capacity, molar heat capacity and calorimeter constant do not vary with temperature.

Approaching calorimetry (and thermodynamics) problems: What LAW should be your guiding principle in the back of your head at all times?

1st Law of thermodynamics

Why temperature intensive?

Since one can have one mole of a substance of 273K, 298K, 313K, etc. 10
Why concentration intensive? I can have 1 drop of 1.0M NaOH
I can have 1 gallon of 1.0M NaOH

Define **intensive property** (and give examples): property that is independent of the amount of a given substance present

2 examples of intensive properties:

- temperature
- concentration

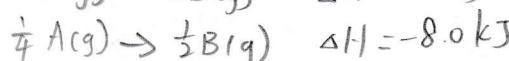
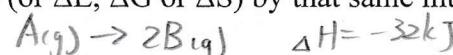
Define **extensive property**: property that depends on the amount of a given substance given.

Think for a second: is energy extensive or intensive? extensive

(Think: 1 gallon of gasoline has a lot more energy than 1 mL of gasoline)

You need to keep this in mind too when doing problems, remembering that ΔH (and ΔE , ΔG , ΔS) values listed in tables are per mole of reaction. If you multiply the coefficients of a reaction by an integer, one must also multiply the ΔH values (or ΔE , ΔG or ΔS) by that same integer.

Different styles of calorimetry problems



No reaction: Calorimetry Problem #1: A 110. g sample of copper ($C_{Cu} = 0.20 \text{ J}/\text{C}^{\circ}\text{g}$) is heated to 82.4°C and then placed in water at 22.3°C. The final temperature of the water and Cu is 24.9°C. What is the mass of water in the container (assuming all heat lost by copper is gained by water)?

Hint #1. No reaction is written, no ΔH data is given. Assume in this type of problem, no reaction has taken place. Hint #2. No calorimeter constant is given, so ignore the calorimeter, although in an actual experiment, you'll wish to determine the calorimeter constant. Hint #3. You must analyze every calorimetry problem thinking about 1st Law, thinking where the energy loss and energy gain lie. Since the total energy of the universe is constant, the energy lost = energy gained!!! **Put a negative sign in front of everything losing energy** and you're set! In this case,

$$m_{Cu} = \text{mass of Cu}$$

$$-q_{Cu} = q_{water} \quad (\text{or, if you prefer, } q_{Cu} + q_{water} = 0)$$

$$-\left(\begin{array}{l} \text{energy lost} \\ \text{by Cu} \end{array}\right) = \left(\begin{array}{l} \text{energy gained} \\ \text{by H}_2\text{O} \end{array}\right)$$
$$-(m_{Cu} \cdot C_{Cu} \cdot \Delta T) = m_{H_2O} \cdot C_{H_2O} \cdot \Delta T$$

$$-(110.9 \cdot 0.20 \text{ J/g.C.} \cdot (24.9^{\circ}\text{C} - 82.4^{\circ}\text{C})) = m_{H_2O} \cdot 4.18 \text{ J/g.C.} \cdot (24.9^{\circ}\text{C} - 22.3^{\circ}\text{C})$$

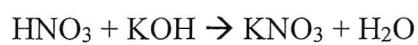
$$m_{H_2O} = 120 \text{ g}$$

Note that the energy required to raise 1g of water 1 degree Celsius corresponds to the calorie.



0.050 mol HNO₃ and 0.060 mol KOH to start

Calorimetry Problem #2 (involving a reaction). Two solutions are mixed in a calorimeter; 100. mL of 0.50 M HNO₃ with 100. mL of 0.60 M KOH at 25.0°C. The temperature increases to 28.5°C inside the coffee-cup calorimeter. Calculate the enthalpy of neutralization in kJ/mol reaction for the reaction below. (Note: Problems asking for the enthalpy are asking for the change in enthalpy.)



Type of calorimeter that indicates constant pressure.

Looking at the amounts of reactants here, what alarm bells should be going off in your head?

Thinking about limiting reagent is important when one has 2 or more reagents present.

Always think about the 1st Law: Energy lost = energy gained

Ask yourself: where's the energy gain? where's the energy loss?

Energy Gain?	temperature increase of solution	}	temperature increase in surroundings	energy loss in the system
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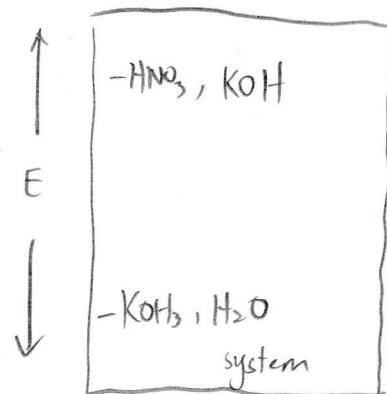
Set up your energy lost = energy gained mathematical equation (NEGATIVE SIGN in front of ENERGY LOST!!!)

$$-(\text{energy lost due to reaction}) = \text{energy gained by solution increasing in temperature} \quad \Delta H = q_p$$

$$-(\Delta H) = m_{\text{solution}} \cdot C_{\text{solution}} \cdot \Delta T$$

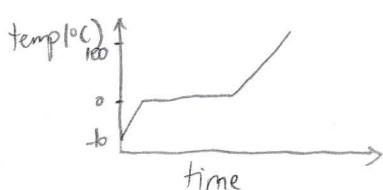
$$\Delta H = -200. \text{ g} \cdot 4.18 \text{ J/g}\cdot\text{°C} \cdot (28.5^\circ\text{C} - 25.0^\circ\text{C})$$

$$\Delta H = \frac{-2.93 \text{ kJ}}{0.050 \text{ mol reaction}} = \boxed{-59 \frac{\text{kJ}}{\text{mol}} = \Delta H}$$



Hint #1 For aqueous solutions, even though it is sometimes a brute approximation, unless a specific heat capacity for the aqueous solution is given, use the specific heat capacity of liquid water 4.18 J/g*°C. Hint #2 Assume no variation of heat capacities or ΔH with temperature.

Hint #3 In this problem, we have no calorimeter constant, so we ignore heat lost/gained by the calorimeter. Hint #4 While masses of solutes in the solution are considered if known (and this includes a solute in the process of being dissolved), in this case, the mass of the solvent was not given and consequently the density of the solution is unknown; in such cases, one can assume the density of the solution is 1.00 g/mL for aqueous solutions. Hint #5 One does not use specific heat capacities of solutes in problems.



Heating Curve of H_2O

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Rationalize: the last problem was a strong acid- strong base neutralization.

Always look at the sign of the ΔH , to ask yourself if your choice of exothermic and endothermic makes sense. Strong acids and strong bases are reactive, so will be less stable, higher in potential energy than the water product.

Calorimetry #3. Ice problem (multiple energy loss/gain): An ice cube at -10°C of 3.0 g mass is placed in 360 g water at 20°C . Calculate the final temperature of the water, assuming no heat exchange with surroundings. ($\Delta H_{\text{fus}} = 6.9 \text{ kJ/mol}$; $s_m \text{ ice} = 38 \text{ J/mol}\cdot\text{K}$; $s_m \text{water(l)} = 75 \text{ J/mol}\cdot\text{K}$)

#1. Attack problem. Always think about the first Law of thermodynamics! Heat loss= heat gain. Think: there's much more water than ice; consequently, that ice is going to melt completely. Outline the steps of the heat loss and the heat gain.

Heat gain

- ① ice goes from -10°C to 0°C
- ② ice melts
- ③ former ice (now liquid H_2O) goes from 0°C to T_f

Heat loss

- ① Warm H_2O goes from 20°C to T_f

#2. Now solve the math problem (with numbers): one equation, one variable. Word of advice: keep track of units! Dimensional analysis prevents unit errors!!!!

$$-(\text{energy loss by warm } \text{H}_2\text{O as heat}) = \text{energy gain by ice.} \quad 3.0 \text{ g ice} = 0.167 \text{ mol ice} \quad 360 \text{ g water} = 20 \text{ mol water}$$

$$-\left(n_{\text{warm H}_2\text{O}} \cdot s_m(\text{warm H}_2\text{O}) \cdot \Delta T\right) = \underbrace{n_{\text{ice}} \cdot s_m(\text{ice}) \cdot \Delta T}_{\text{step ①: of heat gain by ice above}} + \underbrace{n_{\text{ice}} \cdot \Delta H_{\text{fus}}}_{\text{step ②: of heat gain by ice}} + \underbrace{n_{\text{ice}} \cdot s_m(\text{H}_2\text{O(l)}) \cdot \Delta T}_{\text{step ③: of energy gain by ice}}$$

$$-(20 \text{ mol} \cdot 75 \text{ J/mol}\cdot\text{°C} \cdot (T_f - 20^\circ\text{C})) = \underbrace{\left(0.167 \text{ mol} \cdot 38 \text{ J/mol}\cdot\text{°C} \cdot 10^\circ\text{C}\right)}_{\text{step ①}} + \underbrace{\left(0.167 \text{ mol} \cdot 6900 \text{ J/mol}\right)}_{\text{step ②}} + \underbrace{\left(0.167 \text{ mol} \cdot 75 \text{ J/mol}\cdot\text{°C} \cdot (T_f - 0^\circ\text{C})\right)}_{\text{step ③}}$$

$$\boxed{T_f = 19^\circ\text{C}}$$

Bomb calorimeter:

One can do reactions in a rigid steel container (known as the “bomb” of the bomb calorimeter); this is a way of doing reactions under **constant-volume** conditions. These are used in labs to determine the number of calories per serving that are seen on labels of food items.

Important: under constant volume conditions, what is $\Delta E = ?$ (show q+w calc.)

$$\left. \begin{array}{l} \Delta E = qv + w \\ \Delta E = qv - P\Delta V \\ \boxed{\Delta E = qv} \end{array} \right\} \text{At constant volume} \quad \Delta V = 0 \text{ in the bomb}$$

\rightarrow This claim means $\Delta E / C_{cal}$ food calories
if the manufacturer didn't lie.

Example: A new diet dessert claims it has fewer than 10 food calories per serving. One serving was tested in a bomb calorimeter and burnt in oxygen and the temperature increased by 4.937°C . Did the manufacturers lie? ($C_{cal} = 8.151 \text{ kJ/K}$) ($C_{cal} = 8.151 \text{ kJ/K} = 8.151 \text{ kJ}^\circ\text{C}$)

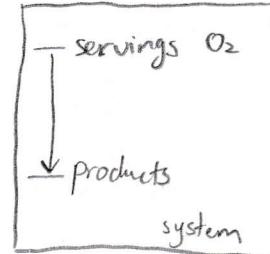
- energy loss = energy gain
due to reaction due to temperature
(in system) increasing of calorimeter
(as heat)

The manufacturer
didn't lie

$$-(\Delta E) = C_{cal} \Delta T$$

$$\Delta E = -(8.151 \text{ kJ}^\circ\text{C}) (4.937^\circ\text{C})$$

$$\Delta E = -40.2 \text{ kJ} \times \frac{1 \text{ food calorie}}{4.18 \text{ kJ}} = -9.6 \text{ food calories} = \Delta E$$



Note: 1. The bomb calorimeter contains water that surrounds the bomb. Your book IN MOST CASES gives problems where the calorimeter constant has already accounted for the water inside the calorimeter. Since no amount of water is given in the problem, assume that the calorimeter constant takes into account not only the steel container but also the water present inside the bomb calorimeter. 2. Assume in problems where a bomb calorimeter is used that given its massiveness, that the bomb calorimeter absorbs all heat released by an exothermic reaction.

Note how the bomb calorimeter is useful for directly calculating ΔE and a coffee-cup calorimeter is useful for directly calculating ΔH .

$C_{empty \text{ calorimeter}} = C_{bomb \text{ w/o water}} = C_{empty \text{ bomb}}$ = the calorimeter constant for the calorimeter minus the water that is added to the bomb calorimeter. If a problem gives a C_{bomb} and says that water is added to the bomb, you may assume that the C_{bomb} refers to the $C_{empty \text{ bomb}}$. Otherwise, assume that C_{bomb} refers to the calorimeter constant for the bomb calorimeter with the water in it.

So, if $C_{bomb} = 6.00 \text{ kJ/K}$ and it is stated that 1.00 kg water is then added to the bomb, what is the C_{cal} with the water inside?

$$C_{cal} (\text{for bomb with } H_2O) = C_{bomb} (\text{with the } H_2O \text{ inside}) = C_{empty \text{ bomb}} + m_{H_2O} \cdot (C_{H_2O})$$

$$\boxed{10.18 \text{ kJ/K}} = 6.00 \text{ kJ/K} + (1.00 \text{ kg}) \cdot (4.18 \text{ kJ/g} \cdot \text{K})$$

Lecture Concepts 4. Change in Enthalpy from Collected Data: Hess's Law, Standard Enthalpies of Formation, Bond Energy Data

We've learned how to calculate ΔH from a calorimetry experiment; the ΔH for a given reaction may also be calculated from other known ΔH values by doing what are known as Hess's Law problems.

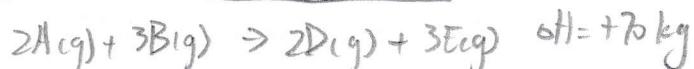
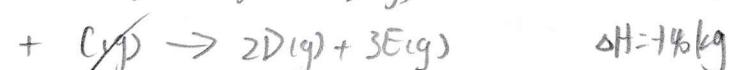
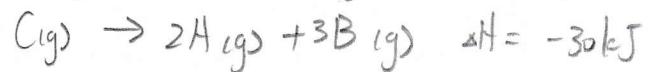
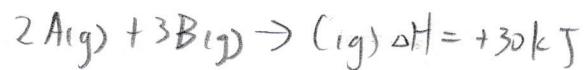
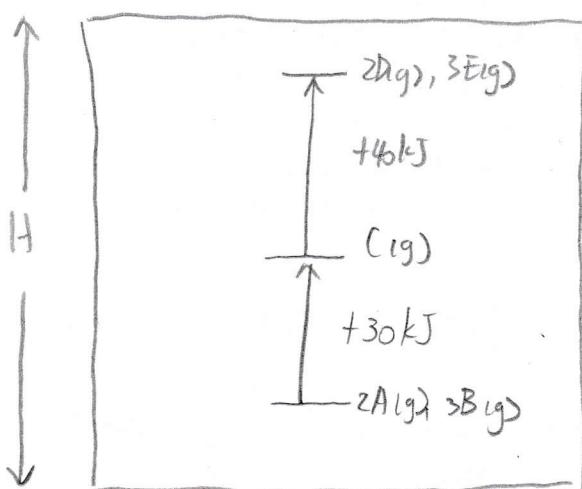
(H)

Two facts are going to be important for Hess's Law problems. 1. Enthalpy is a state function and 2. Enthalpy is an extensive property.

Hess's Law states that: The enthalpy change for any reaction depends on the products and reactants and is independent of the pathway or number of steps between reactant and product.

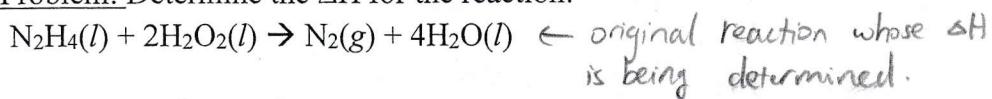
Three things to keep in mind for Hess's Law problems:

1. If a reaction is reversed, the sign of ΔH is also reversed. (Draw potential energy diagram to consider why.)
2. The magnitude of ΔH is directly proportional to quantities of reactants and products in a reaction. That is, if coefficients in a balanced reaction are multiplied by an integer, ΔH is also multiplied by this integer. This is true since ΔH is an extensive property.
3. If 2 reactions are added, their ΔH s are also added. (Confer with potential energy diagram below.)

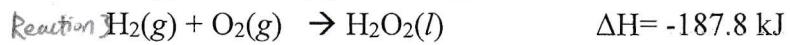
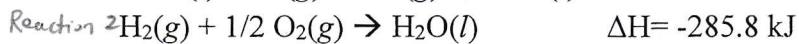


Note: That one can do Hess's Law type problems with other thermodynamic functions that are state functions and extensive properties, such as ΔE (and ΔG and ΔS when we see those). Simply replace all ΔH in the instructions in the three considerations above with ΔE (or ΔG or ΔS , as appropriate).

Hess's Law Problem: Determine the ΔH for the reaction:



Given the following data: Reaction 1 $\text{N}_2\text{H}_4(l) + \text{O}_2(g) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l)$ $\Delta H = -622.2 \text{ kJ}$



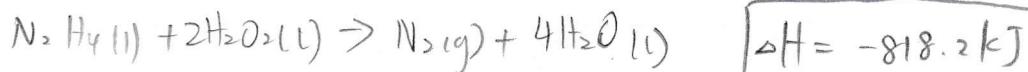
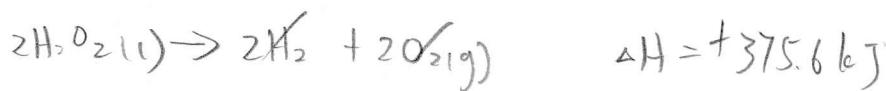
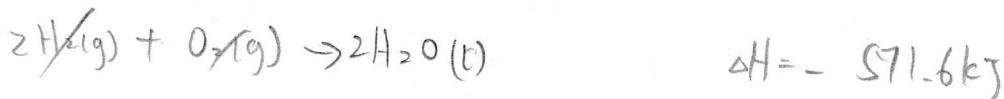
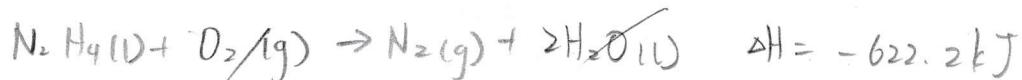
shift

Pieces of advice:

1. Notice if any of the reactants or products of the original reaction are only in ONE of the reactions in the data set. Then switch the sign and multiply by coefficients accordingly.
2. Beware of bogus ΔH values; sometimes on exams, you'll only use SOME of the data given.

Solve:

1. Think: Which chemical equation(s) in the data set will we have to reverse (and therefore switch the sign)? In which cases do we multiply the ΔH by a coefficient?



standard enthalpy of formation = standard heat of formation

Standard Enthalpies of formation to Determine the ΔH°_{rxn}

this means that in the chemical equation associated with ΔH°_f the coefficient of the product is 1
 For a given substance, the **standard enthalpy of formation** = ΔH°_f = the change in enthalpy accompanying the formation of **one mole** of a given substance from the elements that make up that substance, such that those elements are in their standard state.

What does the degree symbol mean after a thermodynamic function?

Means that all reactants & products are in their standard state
 Define the standard state for compounds:

For a gas: Gas at 1 atm pressure

For a solute in solution: Solute is at 1 M concentration

For compound (liquid or solid): use liquid or solid as is.

Standard state for an element: form of that element that exists most stably at 298 K and 1 atm external pressure.

Give the standard state for nitrogen, bromine, iodine, chlorine, fluorine, copper, mercury, carbon, phosphorus, and sulfur.

$N_2(g)$, $Br_2(l)$, $I_2(s)$, $Cl_2(g)$, $F_2(g)$, $C(s)$, $Hg(l)$,

(s , graphite), $P_4(s$, white) = $P(s$, white)

$S_8(s$, rhombic) = $S(s$, rhombic)

All metals are monoatomic
↓ in their standard form

All metals but one

are solid in standard state.

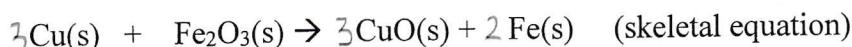
What is the standard enthalpy of formation for all of the elements in their standard state? $\Delta H^\circ_f = 0 \text{ kJ/mol}$.
 memorize the above value $Br_2(l) \Rightarrow Br_2(l) \quad \Delta H = 0 \text{ kJ/mol}$

Using Hess's Law and standard enthalpies of formation, one can find standard heats of reaction (standard heat of reaction = $\Delta H^\circ = \Delta H^\circ_{rxn}$).

standard enthalpy of formation what is written after ΔH° value is the product of the reaction associated with ΔH°_f .

Problem: Given $\Delta H^\circ_f(Fe_2O_3(s)) = -824.2 \text{ kJ/mol}$ and the $\Delta H^\circ_f(CuO(s)) = -157.3 \text{ kJ/mol}$.

Calculate the heat of reaction when copper is heated with iron (III) oxide.

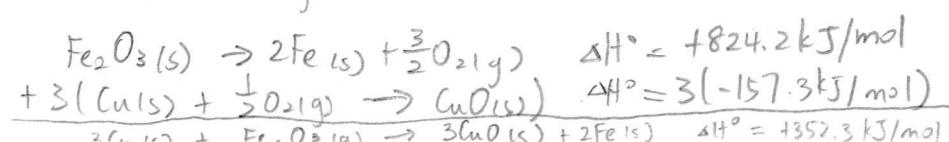


Write the equations corresponding to the standard enthalpies of formation (ΔH°_f) of the above substances, then solve the problem using Hess's Law.

Chemical equation associated with the ΔH°_f of $Fe_2O_3(s)$



Chemical equation associated with the ΔH°_f of $CuO(s)$



However, while one may use a Hess's Law type approach, a quick approach is to use the following equation, which takes into account any multiplications by coefficients and switches the sign of the reactants (which in the standard heat of formation equation are on the product side of the equation). ΔH° values

$$\Delta H^\circ_{rxn} = \sum n_p * \Delta H^\circ_f(\text{products}) - \sum n_r * \Delta H^\circ_f(\text{reactants})$$

n_p = coefficient in front of the product; n_r = the coefficient in front of the reactant.

From math, what is meant by Σ ? *summation*

Let's consider a generic reaction $iA + jB \rightarrow kC + mD$ (where i, j, k and m are coefficients, A and B are reactants, C and D are products); show how to calculate the ΔH°_{rxn} from the standard enthalpies of formation.

$$\Delta H^\circ_{rxn} = [k \cdot \Delta H^\circ_f(\text{of } C) + m \cdot \Delta H^\circ_f(\text{of } D)] - [i \cdot \Delta H^\circ_f(\text{of } A) + j \cdot \Delta H^\circ_f(\text{of } B)]$$

Where does one find ΔH°_f values when doing problems in your textbook at home?

Appendix in Zumdahl textbook
What about on an exam?

ΔH°_f values are given
Should you memorize standard enthalpy of formation values?

no except know that $\Delta H^\circ_f = 0 \text{ kJ/mol}$
for element in its standard form

Now, let's apply this equation to the problem on the previous page: Given $\Delta H^\circ_f(\text{Fe}_2\text{O}_3(s)) = -824.2 \text{ kJ/mol}$ and the $\Delta H^\circ_f(\text{CuO}(s)) = -157.3 \text{ kJ/mol}$. Calculate the heat of reaction when copper is heated with iron (III) oxide.



$$\begin{aligned}\Delta H^\circ_{rxn} &= [3 \cdot \Delta H^\circ_f(\text{CuO(s)}) + 2 \cdot \Delta H^\circ_f(\text{Fe(s)})] - [3 \cdot \Delta H^\circ_f(\text{Cu}) + \Delta H^\circ_f(\text{Fe}_2\text{O}_3)] \\ &= [3 \cdot 0 \text{ kJ/mol} + 2 \cdot 0 \text{ kJ/mol}] - [3 \cdot 0 \text{ kJ/mol} + 1 \cdot (-824.2 \text{ kJ/mol})] \\ &= +352.3 \text{ kJ/mol.}\end{aligned}$$

Zumdahl Chemistry
Chapter 8 Section 8
Bond Energies to ΔH Calculations

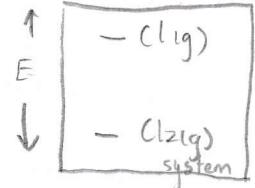
Based on experimental data, bond energies (bond energy = the energy required to break a chemical bond) are calculated. Bond energies have a positive value

Pre-topic thoughts:

1. Is bond-breaking endothermic or exothermic? (Stable) bond forming is...?

endothermic

Example of bond-breaking



2. When referring to tables, would you think O-O single bonds have the same amount of bond energy as O=O double bonds?

No, takes more energy to break O=O double bonds.

3. Suggest an explanation as to why O-O single bonds are weaker than C-C single bonds...

oxygen is a very electronegative atom, each oxygen pulls on the electrons in bond, making bond weak (weak = easy to break)

4. What NYA topic should you be reviewing to do well on a bond energy problem?

Lewis structure

Using bond energies, one can calculate the ΔH° for a given reaction by using the following equation (typically gives a decent approximation of the heat of reaction).

$$\Delta H^\circ = \Sigma D(\text{bonds broken}) - \Sigma D(\text{bonds formed})$$

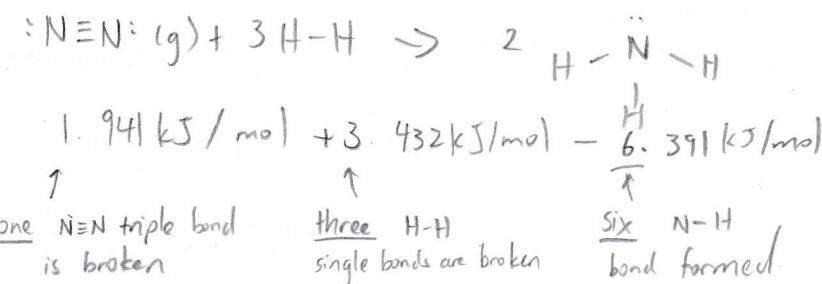
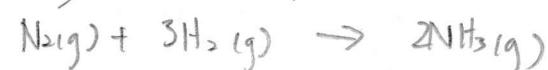
D refers to the bond energy (often shown in kJ/mol)

\leftarrow Bond energy values found in Table 8.4

Problem: Calculate the ΔH° of ammonia synthesis from hydrogen and nitrogen gases (in kJ/mol) from the following bond energy data: N-N 163 kJ/mol N=N 418kJ/mol N≡N 941 kJ/mol

H-H 432 kJ/mol N-H 391 kJ/mol \rightarrow 5 valence e⁻s $\times 2$ = 10 valence e⁻s in N_2

In such problems a reaction must be given to you



$$\boxed{\Delta H^\circ = -109 \text{ kJ/mol}}$$

This bond energy equation to determine heat of reaction should be used only for gases... why?

(Warning: Some textbooks occasionally erroneously use it with liquids...)

{ Solids, liquids have intermolecular forces that are breaking/forming (in addition to covalent bonds breaking/forming) during reaction

Chapter 17 Zumdahl Chemistry

Lecture Concepts 5. Intro to Spontaneity and Entropy

Define: **spontaneous process (or spontaneous reaction):** = process (or reaction) that occurs without external intervention
 Examples of such intervention:
 ① electricity running through a wire
 ② another reaction (not reaction in definition)

Thoughts of the moment:

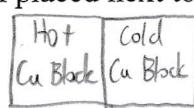
- When we talk about spontaneous processes, we say that such and such a process is spontaneous AT A GIVEN TEMPERATURE. Sometimes, reactions will be spontaneous at higher temperatures but not at lower temperatures and vice-versa.
- If we say a reaction is spontaneous as written, this means the forward reaction will occur MORE than the reverse reaction (but the reverse reaction may occur to some extent). Consider the following example $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$; is this SPONTANEOUS at 28°C, knowing that water vapour is present above liquid water at this temperature from the previous course? Why or why not?
 No, since $\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l)$ (reverse reaction) will occur better at 28°C, since 100°C is the boiling point of H₂O
 (Assume 1 atm external pressure for this equation)
- Does exothermic mean the same thing as spontaneous?
 No, there are endothermic processes that occur spontaneously
- Does spontaneous indicate something about the speed of the reaction?
 No, spontaneous processes may occur slowly or quickly

Think about the following examples in the following context: one direction of a reaction is SPONTANEOUS while reverse direction is NON-SPONTANEOUS.

The vaporization of water at 28°C.

Not spontaneous (see explanation)

Hot copper block placed next to cold copper block (direction of heat flow).



will the heat flow spontaneously from hot block to cold block?

Yes, since forward process occurs

better than reverse process

(Reverse process would have hot block getting hotter and cold block getting colder)

Does pure iron to rust spontaneously?

Yes, rust never goes back pure iron in H₂O.

So what governs the spontaneity of processes? Second Law of thermodynamics

Define Second Law of Thermodynamics.

The entropy of the universe is always increasing.

Which begs the question: what is entropy?

Write some ways of thinking about entropy (entropy = S).

3 non-scientist
entropy definition

- ① disorder
- ② randomness
- ③ chaos

3rd thermodynamic
function we've seen
in this course

Scientific
entropy definitions:

As Entropy increases, these increase

- ① positional probability
- ② dispersal
- ③ number of microstates

So, consider: the driving force for a spontaneous process is an increase in entropy of the universe. Be CAREFUL that you do not confuse entropy of a system with entropy of the universe!!!

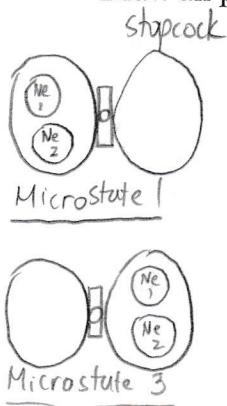
Let's consider a physical example: Imagine a jar with two layers of marbles; the lower layer is green marbles, the upper layer is red marbles. You overturn the jar and set it upright. Will the lower layer be green marbles and the upper layer red marbles? (Think about from an ENTROPY point of view.) Green & Red marbles would be mixed after overturning the jar most likely because it's more probable in terms of position of marble.

Now consider a process: Effusion, The Expansion of a Gas Into an Evacuated Chamber

Imagine a 2-bulbed piece of glassware separated by a stopcock.

Define microstate = arrangement of a particular configuration

- Imagine there are two neon gas atoms in one bulb (which we'll label as microstate I); the stopcock is opened. Label one neon atom with a shaded circle and the second neon atom with an unshaded circle.
- Draw all possible microstates and then state which is the most probable microstate.



$\frac{1}{4}$ probability that Ne atoms remain in the left bulb (no effusion)

$\frac{1}{2}$ probability that Ne atoms are evenly distributed in the two bulbs (Microstate 2 & 4)

Probability of No Dispersal (all particles remain in left bulb in case of effusion)

For 1 molecule of gas	$\frac{1}{2^1}$
2 molecules	$\frac{1}{2^2}$
3 molecules	$\frac{1}{2^3}$
6 molecules	$\frac{1}{2^6}$
n molecules	$\frac{1}{2^n}$

- Nature proceeds toward the most probable states in terms of particle position, which is referred to as the state of greatest positional probability (greatest positional probability = existence of most microstates!). This gives us a rationale for the effusion of gas and a more even distribution of particles through the container (the two-bulbed glassware here).
- For this, the example of gas effusion, the entropy of the system increases, nothing happens to the entropy of the surroundings (as we'll see, a change in entropy of the gas particles for surroundings requires a change in enthalpy from a reaction or change of phase), so therefore the entropy of the universe increases.
- CAUTION: In the case of effusion, since nothing is happening to the entropy of the surroundings, an increase of entropy of system = increase in entropy of universe. An increase of entropy of the system however, does not necessarily mean an increase in entropy of the universe, since there are two parts of the universe: system and surroundings.

A = substance ← imagine substance
is the system

Entropy of system for solid vs. liquid vs. gas (Make drawings below.)

A(s) A(l) A(g)
lowest entropy highest entropy
of system of system

Is $\text{CO}_2(\text{g}) \rightarrow \text{CO}_2(\text{s})$ ever spontaneous? Yes. (at low enough temperatures) since

system if the entropy of system is decreasing during this process, the entropy of the surroundings must be a reaction Consider: entropy of system for carbon (graphite) vs. carbon (diamond) increasing to a greater extent is occurring includes reactants & products C(s, graphite) ← carbon particles are very rigid in terms of position C(s, diamond) ← smaller entropy of system in diamond

to compensate for this process to be spontaneous

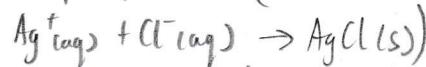
Consider: entropy of system of $\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g})$

entropy of system increases for this reaction

When there are more moles of gas on the product side of the equation relative to the reactant side of the equation, the entropy of the system is said to increase since gas particles fill a container better. When there are fewer moles of gas on the product side of the equation relative to the reactant side, the entropy of the system is said to decrease.

This paragraph
always holds true.

During a precipitation, such as



entropy of system is decreasing.

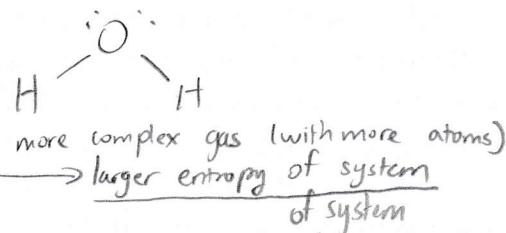
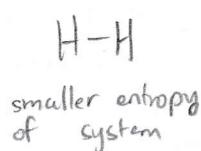
In an exam,
assume you
have one of
this overwhelming
majority of
cases!

In an overwhelming majority of cases of reactions that don't involve gases, as the number of aqueous solutes increases as a reaction proceeds, there is an increase in the entropy of the system. Similarly, as the number of aqueous solutes decreases for such reactions, there is a decrease in the entropy of the system. So, for example, there is an increase of entropy of the system as an ionic solid is dissolved. $\text{NaNO}_3(\text{s}) \xrightarrow{\text{in H}_2\text{O}} \text{Na}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$

The entropy of system increases in above process.

(There are some exceptions to the above paragraph, such as $\text{HF}(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{F}^-(\text{aq})$ where the entropy of the system decreases as the reaction occurs. This is thought to be due to a certain amount of order being created as the water molecules solvate the ions that are formed. Consider this particular example, however, to be an unusual case.)

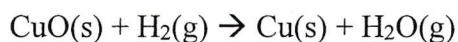
Thinking together: Which has a more positive entropy of system, hydrogen gas or water vapour? From point of view of vibrational, rotational motion (and electrons).... (Draw Lewis structures below)



When looking at a system, a more complex gas has a greater entropy than a less complex gas. However, when comparing the entropy of the system for a reaction, one should only look at the complexity of gas particles when the number of moles of gas is the same on both sides of the equation.

entropy of system increasing = ΔS is a positive number

In which direction (reverse or forward) will the change in the entropy of the system ΔS be positive for the below reaction? (Note that if you see S with no subscript that it refers to entropy of the system.)



The ΔS of the reaction is increasing and same number of we can rationalize this since $\text{H}_2\text{O}(\text{g})$ gas on both sides of equation is more complex than $\text{H}_2(\text{g})$

State the **Third Law of Thermodynamics**.

zero is the lowest possible value of entropy

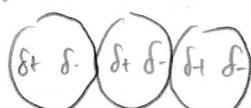
The entropy of system is zero for a perfect crystal at zero Kelvin

Make a sketch to add to your understanding of how the Third Law of Thermodynamics relates to entropy (why that temperature? why crystal?).

Crystal = highly ordered solid

Imagine we have a crystal containing a polar molecule.

Imagine we have a polar molecule particle



in each circle s.t. the $\delta+$ and $\delta-$ portions of the molecules are aligned as above

While all it is important for you to grasp in this course is a general sense of entropy (probability, dispersion, randomness), there is a mathematical definition of entropy as well:

You're not responsible for all in italics below although it'll give you a sense of where raw numbers come from, from where future equations are derived from:

$S = k * \ln \Omega$ where Ω refers to the number of microstates accessible to a substance, k is the Boltzmann constant ($R/\text{Avogadro's number} = k$ so S has units of J/K therefore).

For two different microstates: $\Delta S = k * \ln \Omega_1 - k * \ln \Omega_2 = k * \ln(\Omega_1 / \Omega_2)$ or alternately expressed as $\Delta S = nR \ln(V_2/V_1)$; think: increasing the volume increases the microstates.

To see where some equations seen for ΔS come from, it helps to imagine we're looking at what's called a reversible (i.e., changes in volume are done in infinitesimally small increments) isothermal (i.e., constant temperature) expansion.

- $\Delta E = 0$ in this scenario (no reaction). ($q_{\text{rev}} = \text{reversible heat}$)
- Therefore, $q_{\text{rev}} = -w_{\text{rev}}$ (q_{rev} means infinitely small changes in heat are made).
- $w_{\text{rev}} = -pdV$ (from calculus showing incremental changes is done with dV , not ΔV .)
- Rearrange above with Ideal Gas Law, get $w_{\text{rev}} = -nRTdV/V$
- Integrate \int on both sides of equation; get $w = -nRT \ln(V_2/V_1)$; $q = nRT \ln(V_2/V_1)$
- Therefore $dS = q_{\text{rev}}/T$; small changes in heat are $nC_m dT$ (C_m is molar heat capacity, constant P) \leftarrow units of J/K $\Delta S = \text{infinitely small}$
- $dS = nC_m dT/T$ or $\Delta S = nC_m \ln(T_2/T_1)$ \leftarrow Equation by which entropy is calculated.

Lecture Concepts 6. Required Calculations of Free Energy, Entropy of System, Surroundings and Universe In Zumdahl textbook 9th edition in Appendix

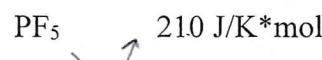
S° is written ΔS°

Standard entropy value = S° = the increase in entropy as a substance is heated from 0K to 298K at 1 atm pressure.

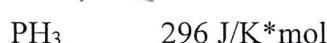
Problem 1, Standard Entropies: Match the Standard Entropy Value (S°) with the Substance



vs.



vs.



Xe(g) has a $S^\circ = 170 \text{ J/K} \cdot \text{mol}$

$\text{XeF}_2(\text{g})$ has a $S^\circ = 254 \text{ J/K} \cdot \text{mol}$

more complex substance has the higher S° value

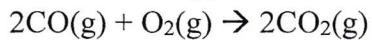
ΔS° = entropy change (of system) during a given reaction
(under standard state condition)

24

Since entropy is a state function and an extensive property (based on the number of moles), one can use an entirely analogous equation to that seen with standard heats of formation to calculate entropy change during a given reaction: $\Delta S^\circ = \sum n_p * S^\circ_{\text{products}} - \sum n_r * S^\circ_{\text{reactants}}$

n_p = coefficient in front of products n_r = coefficient in front of reactants

Problem 2, Standard Entropies. Calculate ΔS° for the following reaction, given the following standard entropy values: CO: 198 J/K*mol; CO₂: 214 J/K*mol; O₂: 205 J/K*mol).



(Before even doing the problem, be sensible here AS ON THE EXAM: what MUST the sign of your change in entropy be for this problem?)

The entropy will be decreasing since there are fewer moles of gas on the product side of the equation relative to the reactant side of the equation.

$$\Delta S^\circ = [2 \cdot 214 \text{ J/K} \cdot \text{mol}] - [2 \cdot 198 \text{ J/K} \cdot \text{mol} + 205 \text{ J/K} \cdot \text{mol}] = -173 \text{ J/K} \cdot \text{mol}$$

\uparrow
 $S^\circ \text{CO}_2$

$$\Delta S^\circ = -173 \text{ J/K} \cdot \text{mol}$$

Note: Looking in tables you'll notice that S° values for aqueous ions in some cases appear to contradict the 3rd Law of Thermodynamics (which is by the way, impossible). For example, H₃O⁺(aq) has an S° of 0 J/K*mol and some ions are listed with a negative standard entropy. This does not mean that some aqueous ions have less entropy than a perfect crystal at zero Kelvin. All this means is that the standard entropy values given for aqueous ions are compared to that of the hydronium ion, which was arbitrarily given a value of 0 J/K*mol. Since there always has to be more than one aqueous ion in a balanced equation for an equation with aqueous ions, one is always looking at the relative entropies of ions when calculating ΔS° .



ΔS_{univ} is positive when entropy of universe is increasing; this increase is necessary for a spontaneous process.

Determining the change in entropy of universe and surroundings

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{univ}} \text{ (Identify each thermodynamic function)}$$

$S_{\text{univ}} = \text{entropy of universe}$

$S_{\text{surr}} = \text{entropy of surroundings}$

$S = S_{\text{sys}} = \text{entropy of system}$

If ΔS_{univ} is positive for a particular process/reaction, what is true?

process / reaction is spontaneous

If ΔS_{univ} is negative for a particular process/reaction, what is true?

process / reaction is non-spontaneous as written, but will be spontaneous in the reverse direction

If $\Delta S_{\text{univ}} = 0$ for a particular process/reaction, what is true? reverse direction
process / reaction is spontaneous in neither the forward direction nor the reverse direction
(A is a substance)

What is ΔS_{univ} equal to in scenarios a), b) and c) below?

a) Above the melting point for $A(s) \rightarrow A(l)$ (or above the boiling point for $A(l) \rightarrow A(g)$)

(for solid A)

b) Below the melting point for $A(s) \rightarrow A(l)$ (or below the boiling point for $A(l) \rightarrow A(g)$)

ΔS_{univ} will be negative

c) At the melting point for $A(s) \rightarrow A(l)$ (or at the vaporization point for $A(l) \rightarrow A(g)$)

$\Delta S_{\text{univ.}} = 0 \text{ J/K.mol}$

Note again: If you ever see ΔS with no subscript, assume it means change in entropy OF THE SYSTEM.

Melting point for substance A = temperature at which $A(s)$ and $A(l)$ can coexist indefinitely

- Clearly, temperature has an effect on spontaneity of processes/reactions, the required positive nature of the entropy of the universe: yet for $A(s) \rightarrow A(l)$ and $A(l) \rightarrow A(g)$ the change in entropy of the system is positive! How then must temperature come into play?

Entropy of Surroundings:

Write the equation for ΔS_{surr} .

$$\Delta S_{\text{surr}} = \frac{-\Delta H}{T}$$

The temperature is seen in the equation for ΔS_{surr} .
minus sign
 $T = \text{temperature (in unit of K)}$
so always a positive value

Why this equation? In an exothermic reaction, the entropy of the surroundings is increasing since the random motions of the particles surrounding increases (due to, for example, an increase in temperature or a phase change that results as a result of the reaction). In an endothermic reaction, the entropy of the surroundings is decreasing since the random motions of the particles surrounding decreases (due to, for example, a decrease in temperature).

Why is ΔS_{surr} inversely proportional to temperature? Think: molecular motion of the surroundings is less at lower temperatures. Analogy: Just as the energy from the impact of a rock with still water causes a greater change in the random motions (and entropy) of the water than it would with rougher waters, similarly energy released or absorbed by a reaction has a greater impact on the surroundings' random motions at lower temperatures.

↓
fourth thermodynamic function
seen in the course.

Free Energy

Free energy = Gibbs Free Energy = $G = H - T \cdot S$

H = enthalpy (of system)
T = temperature (in K)
 S = entropy (of system)

Write an equation for change in Gibbs' Free Energy at a given temperature.

$\Delta G = \Delta H - T \Delta S$

← useful equations in problems

Now multiply both sides of the equation by $-1/T$.

$$\frac{-\Delta G}{T} = \frac{-\Delta H}{T} + \Delta S = \Delta S_{\text{sur}} + \Delta S_{\text{sys}}$$

What is the left side of the equation equal to?

$$\frac{-\Delta G}{T} = \Delta S_{\text{sur}}$$

Therefore if ΔG is positive, what is true about the spontaneity of the reaction (as written, at that temperature)? If ΔG is positive for a reaction, the reaction is said to be endergonic.

The reverse reaction is spontaneous if the forward is non-spontaneous.

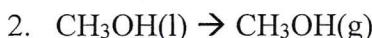
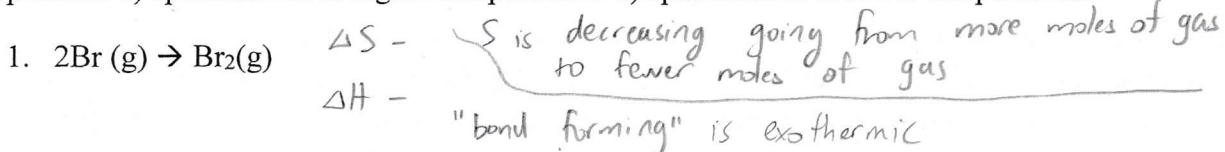
If ΔG is negative, what is true about the spontaneity of the reaction (as written, at that temperature)? If ΔG is negative for a reaction, the reaction is said to be exergonic. reaction is spontaneous

IF...	
ΔS positive and ΔH negative	Process is spontaneous at ... all temperatures
ΔS positive and ΔH positive ΔG is only negative at higher T	Process is spontaneous at... at higher temperatures
ΔS negative and ΔH negative	Process is spontaneous at... at lower temperatures
ΔS negative and ΔH positive ΔG is negative value at no temperature	Process is spontaneous at... no temperature

$$\Delta G = \Delta H - T \Delta S \quad T \text{ (in K) always positive value}$$

Think of examples you know to help you remember the table above: remember.

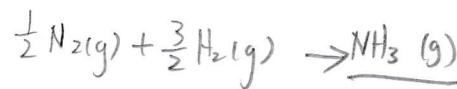
Problem: The following processes are a) spontaneous at all temperatures b) spontaneous at no temperature c) spontaneous at higher temperatures d) spontaneous at lower temperatures.



*$\Delta S +$ S is increasing going to more moles of gas
 $\Delta H +$ since intermolecular forces are broken*

Note: At higher temperatures does not mean higher relative to you; it only means there's a temperature at which the reaction is spontaneous higher than a temperature at which reaction is not spontaneous. Similarly, at lower temperatures means there's a temperature at which reaction is spontaneous lower than a temperature at which reaction is not spontaneous.

Reaction associated
with ΔG_f° for $\text{NH}_3(g)$



Calculating Standard Free Energy Changes:

Standard free energy change (of reaction) = $\Delta G^\circ = \Delta G^\circ_{\text{rxn}}$ The change in free energy for a given reaction such that all reactants and products are in their standard states.

Values found in Appendix 4 (standard)

↓ coefficient of substance
product must be 1

Standard free energy of formation = ΔG_f° = The change in free energy to make **1 mole** of a given substance from the elements that make up that substance, such that those elements are in their standard states.

What is the ΔG_f° for an element in its standard state? $\Delta G_f^\circ = 0 \text{ kJ/mol}$ for such an element

For now, there are 3 ways we've learned to calculate the standard free energy change (one more method after the equilibrium chapter). T = temperature (in Kelvin units)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

ΔS° = change in entropy for a reaction (under standard state condition)
 ΔH° = change in enthalpy for a reaction

2. A Hess's Law approach works with other ΔG° data for reactions that add up to the desired reaction. Why? G is an extensive property

3. $\Delta G^\circ_{\text{rxn}} = [\sum n_p \Delta G_f^\circ_{\text{products}}] - [\sum n_r \Delta G_f^\circ_{\text{reactants}}$] an analogous equation as that seen for standard heats of formation. n_p = coefficients of product n_r = coefficients of reactants

Problem: For the vaporization of water, if $\Delta H^\circ_{\text{vap}} = 4.07 \times 10^4 \text{ J/mol}$ and $\Delta S^\circ = 109 \text{ J/K}^\circ \text{mol}$, calculate at what temperatures will this reaction be spontaneous as written under standard conditions?



Find the temperature at which ΔG° for the vaporization is equal to zero. At all temperatures higher than this temperature, ΔG° will be a negative value

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$0 = 4.07 \times 10^4 \text{ J/mol} - T \cdot 109 \text{ J/K}^\circ \text{mol}$$

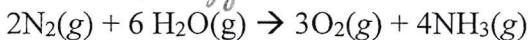
$$T = 373 \text{ K}$$

Answer: at $T > 373 \text{ K}$

↑ Negative ΔG° is when reaction is spontaneous.

Problem: Calculate the standard free energy change for the following reaction given that the ΔG_f° of ammonia is -17 kJ/mol and for water vapour is -229 kJ/mol .

use strategy 3 above



$$\Delta G^\circ_m = [3 \cdot \Delta G_f^\circ(\text{O}_2) + 4 \cdot \Delta G_f^\circ(\text{NH}_3)] - [2 \cdot \Delta G_f^\circ(\text{N}_2) + 6 \cdot \Delta G_f^\circ(\text{H}_2\text{O})]$$

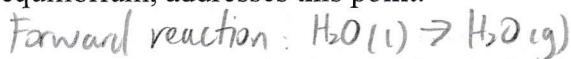
$$\Delta G^\circ_{\text{rxn}} = [3 \cdot 0 \text{ kJ/mol} + 4 \cdot -17 \text{ kJ/mol}] - [2 \cdot 0 \text{ kJ/mol} + 6 \cdot -229 \text{ kJ/mol}]$$

$$\boxed{\Delta G^\circ_{\text{rxn}} = +1306 \text{ kJ/mol}}$$

// End Chapter 17
Sections 1 through 6

Chapter 13 Zumdahl Textbook

Now, the ΔG°_{rxn} , no matter how it is calculated, tells us whether a reaction is spontaneous as written. For example, one mole of liquid water will spontaneously convert to one mole of water vapour above 373 K. However below that temperature, some vapour pressure exists, so clearly the forward reaction occurs to a small degree when it's nonspontaneous as written. The next topic, equilibrium, addresses this point.



Lecture Concepts 7. Introduction to Chemical Equilibrium

From the first course, think of reactions that you were told went (essentially) to completion:
List 2 dissociations and 3 other types of reactions below:

Reaction that go to complete	<u>Dissociation</u>	<u>Other Types of Reactions</u>
	<ul style="list-style-type: none"> ① Soluble ionic compounds split completely into anions ② A strong acid HX(aq) dissociates completely into $\text{H}^+(\text{aq})$ and $\text{X}^-(\text{aq})$ 	<ul style="list-style-type: none"> ① Reaction of a strong acid with a weak/strong base or reaction of a strong base with a weak/strong acid ② Precipitation ③ Combustion of hydrocarbon

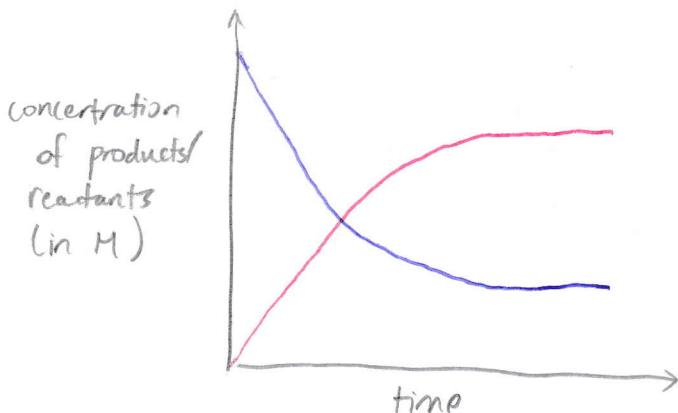
A reaction going to completion is not always the case. Think of 2 dissociations that do NOT go to completion:

- ① A weak acid HK(aq) dissociates only to a small extent into $\text{H}^+(\text{aq})$ and $\text{X}^-(\text{aq})$, weak base B(aq) dissociates to a small extent into $\text{BH}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$
- ② Slightly soluble ionic compounds splitting into cations & anions.

Consider a reaction: $\text{R}_1 + \text{R}_2 \rightarrow \text{P}_1 + \text{P}_2$; R_1, R_2 are gaseous or solute reactants and P_1, P_2 are gaseous or solute products.

The two reactants are placed together in a closed vessel (for purposes of problem-solving, ions in aqueous solutions are thought of as existing in closed vessels (in spite of the slight loss due to vapour pressure of water)) at a given temperature. Whatever the reaction happens to be, after a certain amount of time, it is observed that concentrations of all species (products AND reactants) will remain constant over time. Once these concentrations remain constant over time, the reaction is said to have reached equilibrium or chemical equilibrium.

Sketch concentrations of reactants (I'm arbitrarily making the reactant concentrations equal) and products vs. time. Mark on your graph when the system has reached equilibrium.



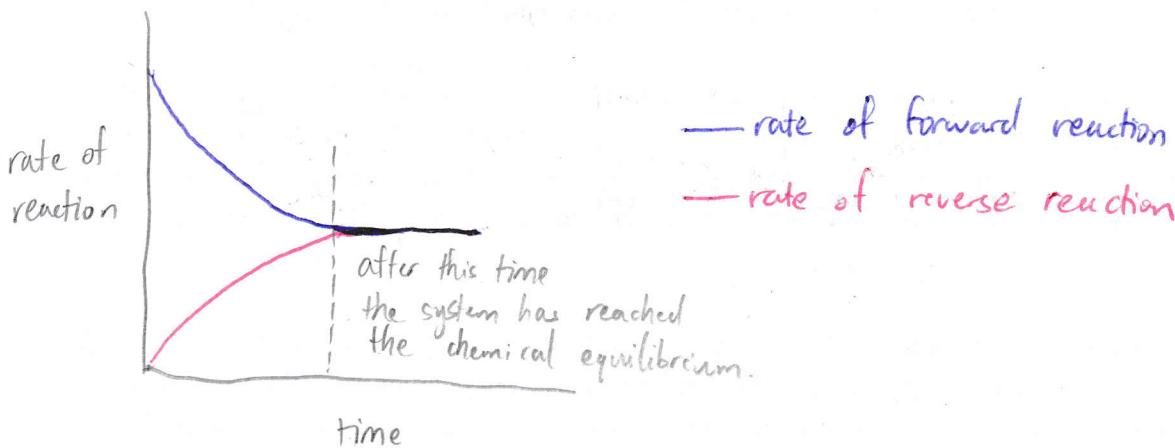
$\begin{array}{l} \xrightarrow{\quad \text{Substance in brackets}^* \text{ means} \\ \quad \text{the substance's concentration} \\ \quad \text{are in M units}} \\ \xrightarrow{\quad [R_1] = [R_2] \quad \leftarrow \text{arbitrary choice to} \\ \quad \text{have reactant concentrations} \\ \quad \text{equal.}} \\ \xrightarrow{\quad [P_1] = [P_2] \quad \leftarrow \text{I made an arbitrary choice to have} \\ \quad \text{more products than reactants at equilibrium}} \end{array}$

Write the reaction on the previous page, but show the arrows one uses to indicate that the system (reactants and products) has reached chemical equilibrium.

Some teachers show arrows to indicate equilibrium these ways:



The concentrations of the reactants and products are constant when the rate of the forward reaction = rate of reverse reaction. Illustrate this making a graph with a legend below: rate of forward and the rate of the reverse reaction. Label on the graph when the system has reached chemical equilibrium.



The concentrations of the reactants and products remain steady over time once the system has reached equilibrium. The fact that the forward and reverse reactions are still occurring at equilibrium is why the equilibrium is called a **dynamic** equilibrium.

One example of experimental evidence for a dynamic equilibrium

Consider that the dissolution of silver iodide has reached equilibrium according to the equation below (dissolving reaches equilibrium immediately upon mixing): $\text{AgI}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{I}^-(aq)$

At equilibrium, the solution above an ionic compound is **saturated**, meaning the maximum concentration of aqueous ions is present in the water above ionic solid. **Water solubility** refers to the maximum concentration is dissolved for a given solid or acid.

Adding solid (we'll discuss why later) does not change the concentration of ions in the saturated solution. However, if one adds some AgI (s) that contains the radioactive isotope I-131, some of the saturated solution will subsequently contain the radioactive aqueous iodide ion. This indicates that the forward reaction is still occurring even though the system is at chemical equilibrium.

Lecture Concepts 8. The Equilibrium Constant and Simple Introductory Calculations

Guldberg & Waage in the late 1800s after experimenting with a variety of reactions came up with the **Law of Mass Action** to describe the equilibrium condition. The Law of Mass Action is a mathematical equation made by setting an equilibrium constant K equal to the mathematical product of all reaction products to the power of their coefficient in the numerator divided by the mathematical product of all reactants to the power of their coefficient in the denominator, such that the reactants and products are at chemical equilibrium. This equation is called the **equilibrium expression** and when we make this equation, we are said to be “applying the Law of Mass Action”. The beauty of this equilibrium constant is that the constant is independent of the starting concentrations or pressures of the initial reactants or products at a given temperature.

For K_c , the reaction products and reaction reactants are given in units of molarity in the Law of Mass Action. For K_p , the reaction products and reaction reactants are given in units of atm in the Law of Mass Action. If you see the equilibrium constant written as K only, you should assume it means K_c (except in the section where we look at the equation $\Delta G^\circ = -RT\ln K$ which we will see later).

Practice: Given the reaction $jA + kB \rightleftharpoons mC + nD$ where j,k,m, and n are reaction coefficients and A,B,C and D are gaseous or solute chemical species, there is an **equilibrium constant K** that describes the reaction system at equilibrium. Write the equilibrium expression for K_c below by applying the Law of Mass Action.

equilibrium \rightarrow expression for reaction above

$$K_c = \frac{[C]^m [D]^n}{[A]^j [B]^k} \stackrel{\substack{\text{Law of Mass Action to describe} \\ \text{equilibrium condition for reaction above}}}{=} K$$

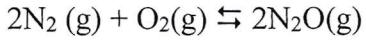
What does the “c” stand for in K_c ? concentration

When you see reactants/products in brackets, what does that mean?

the reactant/product have molarity units

In reactions where gases (and no aqueous solutes) are present, one can express the equilibrium constant as K_p ; what does the p stand for in K_p ? pressure

Problem: Write an equation to express the equilibrium constants K_c and K_p for the following reaction:



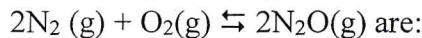
equilibrium expression for K_c for reaction in problem

$$K_c = \frac{[N_2O]_{eq}^2}{[N_2]_{eq}^2 [O_2]_{eq}}$$

↑ equilibrium

$$K_p = \frac{P_{N_2O}^2}{P_{N_2}^2 P_{O_2}}$$

So, if, at a given temperature, the equilibrium concentrations for the reaction



N_2 : 1.40×10^{-4} M, O_2 : 1.25×10^{-5} M and N_2O : 1.00×10^{-2} M

- a) What is the equilibrium constant K or K_c for the reaction above?

$$K = K_c = \frac{[\text{N}_2\text{O}]_{\text{eq}}^2}{[\text{N}_2]_{\text{eq}}^2 \cdot [\text{O}_2]_{\text{eq}}} = \frac{(1.00 \times 10^{-2} \text{ M})^2}{(1.40 \times 10^{-4} \text{ M})^2 \cdot (1.25 \times 10^{-5} \text{ M})} = 4.08 \times 10^8 = K$$

Both answers
are correct

Wait a second! No units!??!! Yes, that's correct. It is perfectly correct to write K_c and K_p with no units. Well, actually, some books still show units for the equilibrium constant, but to be consistent with many books, I'll show with no units too (which assumes for K_c that the concentrations are all in molarity, and for K_p that all the pressures are in atm).

The rationale for no units that you're not responsible for (in italics) is mentioned below for those who are curious:

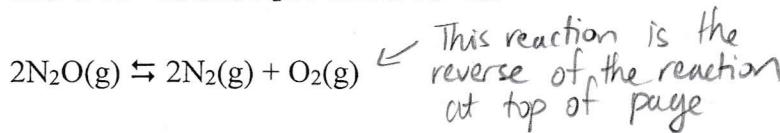
The true Law of Mass Action expression for a reaction $jA + kB \rightleftharpoons mC + nD$ is:

$$(a_C^m \cdot a_D^n) / (a_A^j \cdot a_B^k) = K \text{ where } a \text{ is the activity; } a_A \text{ is the activity of A.}$$

A, B, C, D are substances

And what is the activity? The activity $a = \gamma c$ where γ is the activity coefficient and c is the concentration of each species in molarity. (For example, $a_A = \gamma c_A$.) For ideal gases and solutions of lower concentrations, the activity coefficient $\gamma = 1 \text{ L/mol}$, which multiplied by molarity equals no units. As a result, the law of mass action using concentrations (or pressures in atms) holds effectively for ideal gases and solutions of lower concentrations, ideal gases and solutions of lower concentrations is what we'll concern ourselves with in this course.

- b) Given the same equilibrium concentrations, what is the equilibrium constant (let's call this equilibrium constant K') for the reaction written as below? N_2 : 1.40×10^{-4} M, O_2 : 1.25×10^{-5} M and N_2O : 1.00×10^{-2} M

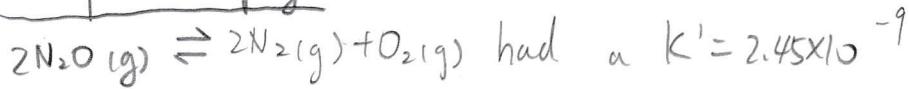


equilibrium expression for reaction above: $K' = \frac{[\text{N}_2]_{\text{eq}}^2 [\text{O}_2]_{\text{eq}}}{[\text{N}_2\text{O}]_{\text{eq}}^2} = \left(\frac{[\text{N}_2\text{O}]_{\text{eq}}^2}{[\text{N}_2]_{\text{eq}}^2 \cdot [\text{O}_2]_{\text{eq}}} \right)^{-1} = K^{-1}$

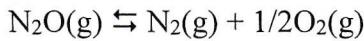
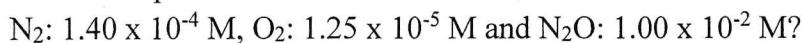
$$K' = (4.08 \times 10^8)^{-1} = 2.45 \times 10^{-9} = K'$$

Devise a general rule: If the equilibrium constant for a reaction in the forward direction is K , then the equilibrium constant K' for the reaction in the reverse direction is equal to K^{-1} .

From previous page



- c) What is the equilibrium constant (let's call it K'') for the reaction written as below, given the same equilibrium concentrations:



$$K'' = \frac{[\text{N}_2]_{\text{eq}} [\text{O}_2]_{\text{eq}}^{\frac{1}{2}}}{[\text{N}_2\text{O}]_{\text{eq}}} = \left(\frac{[\text{N}_2]_{\text{eq}}^2 \cdot [\text{O}_2]_{\text{eq}}}{[\text{N}_2\text{O}]_{\text{eq}}^2} \right)^{\frac{1}{2}} = (K')^{\frac{1}{2}} = (2.45 \times 10^{-9})^{\frac{1}{2}}$$

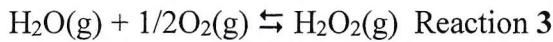
$K'' = 4.95 \times 10^{-5}$

Generally speaking, if you multiply a chemical equation (which has an equilibrium constant K') by any factor n to make a new balanced equation, the equilibrium constant K'' for the new equation is equal to $(K')^n$.

Note: In a), b) and c) on the previous two pages, there was a different equilibrium constant for what was essentially the same reaction. While, at a given temperature, there is only one equilibrium constant, the equilibrium constant however depends on the mathematical equation that is used. The mathematical equation that you use should be the equilibrium expression that is made by using the coefficients in the chemical equation as you see it written.

Problem: Calculate the equilibrium constant K_{c3} for reaction 3 given that the reaction **1** $\text{H}_2\text{O}(g) \rightleftharpoons \text{H}_2(g) + 1/2\text{O}_2(g)$ has a $K_{c1} = 2.36 \times 10^{-19}$ and that reaction **2** $\text{H}_2(g) + \text{O}_2(g) \rightleftharpoons \text{H}_2\text{O}_2(g)$ has a $K_{c2} = 2.3 \times 10^6$.

Reaction 1
plus reaction 2
gives reaction 3



$$(K_{c1}) \cdot (K_{c2}) = K_{c3}$$

$$\left(\frac{[\text{H}_2]_{\text{eq}} [\text{O}_2]_{\text{eq}}^{\frac{1}{2}}}{[\text{H}_2\text{O}]_{\text{eq}}} \right) \left(\frac{[\text{H}_2\text{O}_2]_{\text{eq}}}{[\text{H}_2]_{\text{eq}} [\text{O}_2]_{\text{eq}}} \right) = \frac{[\text{H}_2\text{O}_2]_{\text{eq}}}{[\text{H}_2\text{O}]_{\text{eq}} [\text{O}_2]_{\text{eq}}^{\frac{1}{2}}}$$

In summary, if a reaction 1 (with an equilibrium constant K_{c1}) and a reaction 2 (with an equilibrium constant K_{c2}) add together to make a 3rd reaction, devise a mathematical equation to determine the equilibrium constant K_{c3} for the 3rd reaction:

$$K_{c1} \cdot K_{c2} = K_{c3}$$

Don't confuse equilibrium position and equilibrium constant A = substance

Consider the following data for the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ at a given temperature; what do you think the subscript zero means? $[\text{A}]_0$ = initial concentration of A (in M)

Initial concentrations Equilibrium concs. (M) $K = [\text{NO}_2]^2 / [\text{N}_2\text{O}_4]$

$[\text{N}_2\text{O}_4]_0 = 1.000 \text{ M}$	$[\text{N}_2\text{O}_4]_{\text{eq}} = 0.966$	$K = 4.8 \times 10^{-3}$	↑	experiment 1 above the dashed line
$[\text{NO}_2]_0 = 0.000 \text{ M}$	$[\text{NO}_2]_{\text{eq}} = 0.068$			
$[\text{N}_2\text{O}_4]_0 = 0.000 \text{ M}$	$[\text{N}_2\text{O}_4]_{\text{eq}} = 0.476$	$K = 4.8 \times 10^{-3}$	↓	experiment 2 below the dashed line
$[\text{NO}_2]_0 = 1.000 \text{ M}$	$[\text{NO}_2]_{\text{eq}} = 0.048$			

The **equilibrium position** refers to the equilibrium concentrations (or equilibrium pressures if working with a K_p in a problem); there is an infinite number of possibilities for equilibrium positions for a reaction system at equilibrium that will depend upon the initial concentrations (or pressures). There however is only one equilibrium constant K for a given mathematical equation at a given temperature; this constant is independent of the initial concentrations. The only way to change the equilibrium constant is to change the temperature for a given reaction.

for a given math equation

Converting K_p to K_c and vice-versa: Derivation

Consider a reaction $j\text{A}(\text{g}) + k\text{B}(\text{g}) \rightleftharpoons m\text{C}(\text{g}) + n\text{D}(\text{g})$

From the Ideal Gas Law equation, derive the equation to convert pressure to concentration. If the K_p is in atm, what units of R should we be considering?

$$P = \left(\frac{n}{V}\right) \cdot R \cdot T$$

$$P = C \cdot R \cdot T$$

C = concentration of A (in M)

C = concentration (in M) of a gas

Note for the equation that relates K_p & K_c . I will be using R that has units of atm in it.
 $(R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}})$ (K_p remember hgs pressures of gas in atm)

Write the expression for K_p here for this equation; then plug in the equation above to convert concentrations to pressures.

$$K_p = \frac{P_C^m \cdot P_D^n}{P_A^j \cdot P_B^k} = \frac{(C_C \cdot R \cdot T)^m \cdot (C_D \cdot R \cdot T)^n}{(C_A \cdot R \cdot T)^j \cdot (C_B \cdot R \cdot T)^k} = \frac{C_C^m \cdot C_D^n}{C_A^j \cdot C_B^k} \cdot \frac{(RT)^m \cdot (RT)^n}{(RT)^j \cdot (RT)^k}$$

$$x^m \cdot x^n = x^{m+n}$$

$$\frac{x^{(m+n)}}{x^{(j+k)}} = x^{(m+n)-(j+k)}$$

$$K_p = K_c \cdot (RT)^{(m+n)-(j+k)}$$

In summary, what we see is that $K_p = K_c (RT)^{\Delta n}$ where $\Delta n =$

$\Delta n = \frac{\text{sum of coefficients of the gaseous products minus sum of coefficients of the gaseous reactants.}}$

Problem: Calculate K_p and K_c for the reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$, given the below equilibrium concentrations at 600°C ; SO_2 : 1.50 mol/L; O_2 : 1.25 mol/L; SO_3 : 3.50 mol/L.

Review: Calculate K_c :

$$K_c = \frac{[\text{SO}_3]_{\text{eq}}^2}{[\text{SO}_2]_{\text{eq}} \cdot [\text{O}_2]_{\text{eq}}} = \frac{(3.50\text{ M})^2}{(1.50\text{ M})^2 \cdot (1.25\text{ M})} = \boxed{4.36 \text{ M}^{-1} = K}$$

What's Δn for the equation?

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

$$K_p = 4.36 \text{ M}^{-1} (0.08206 \frac{\text{L atm}}{\text{K mol}}) 873\text{ K}^{-1}$$

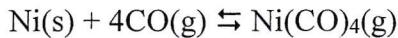
$$K_p = 0.008 \text{ atm}^{-1} \quad \text{or} \quad K_p = 0.008$$

Heterogeneous equilibria problems

Define **homogeneous equilibria**. = equilibrium states such that all reactants & products are in the same phase (phase = state of matter)

Define **heterogeneous equilibria**. = states of equilibrium such that not all reactants and products are in the same phase

Let's consider a heterogeneous equilibria:



You might think that based on the Law of Mass Action that your equilibrium constant (let's call it K') would be $K' = [\text{Ni(CO)}_4]/[\text{Ni}][\text{CO}]^4$; this is not the equilibrium expression that is used however.

Let's say you mixed solid nickel with carbon monoxide gas, what would be happening to the amount of nickel as the reaction proceeds?

moles (amount) of Ni decreases as the reaction occurs

However, nothing is happening to the **concentration** of nickel as the reaction proceeds. Think the density of Ni is 8.91 g/mL and the density doesn't change regardless of how much nickel solid you have. $(8.91 \text{ g Ni/mL Ni}) * (1000 \text{ mL Ni}/1 \text{ L Ni}) * (\text{mol Ni}/58.6 \text{ g Ni}) = 152 \text{ M Ni}$. As was true with nickel, all solids and liquids have a constant concentration throughout a reaction; yes the amounts of solid and liquid can change during a reaction, but the density and therefore the concentration does not.

Density is an intensive property that does not depend upon amount

So, for problem solving purposes, we can replace our solid or liquid concentrations with a constant, since their concentrations do not vary throughout the course of a reaction. The equilibrium constant used for reactions where solids and liquids are present is an equilibrium expression where concentrations of liquids and solids are replaced by the number "1".

$$K' = \frac{[\text{Ni(CO)}_4]_{\text{eq}}}{[\text{Ni}]_{\text{eq}} [\text{CO}]_{\text{eq}}^4} = K' [\text{Ni}]_{\text{eq}} = K \approx \frac{[\text{Ni(CO)}_4]_{\text{eq}}}{[\text{CO}]_{\text{eq}}^4}$$

$[\text{Ni}]$ is a constant value throughout the reaction

What are the only types of substances to be therefore included in the Law of Mass Action mathematical equation?

gases, aqueous solute

Problem: At 800.°C, when the equilibrium pressure of CO=0.236 atm and Ni(CO)₄= 0.414 atm, calculate the K_p and K_c for the reaction: Ni(s) + 4CO(g) ⇌ Ni(CO)₄(g).

$$K_p = \frac{P_{\text{Ni}(\text{CO})_4}}{P_{\text{CO}}^4} = \frac{0.414 \text{ atm}}{(0.236 \text{ atm})^4} = 133.46$$

$$K_p = K_c (R \cdot T)^{\Delta n} \quad \Delta n = -3$$

$$\boxed{K_p = 133 \text{ atm}^{-3}}$$

$$\boxed{K_p = 133}$$

Both answers correct

$$133.46 \text{ atm}^{-3} = K_c (0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \cdot 1073 \text{ K})^{-3}$$

\ll = much less than
 \gg = much greater than

$$K_c = 9.11 \times 10^7 \text{ M}^{-3}$$

$$K_c = 9.11 \times 10^7$$

Both answers are correct.

What is true if K>>1? Think of a reaction or two for which this is true...

When we have a $K > 1$, this means that the reaction goes very close to completion e.g. A precipitation has

When K >> 1, we say the equilibrium lies overwhelmingly to the right.

If K<<1? Think of a reaction or two for which this is true...

If K<<1, we have a small K and there will be mostly reactants present at equilibrium $K < 1$ = the equilibrium lies overwhelmingly to the left

Reaction quotient = Q = mathematical product of all reaction products to the power of their coefficient in the numerator divided by the mathematical product of all reactants to the power of their coefficient in the denominator, but in this case such that initial or non-equilibrium concentrations (or pressures) are used for reactants and reaction products. $Q_c = Q$ where initial or non-equilibrium concentrations (in molarity) are used; $Q_p = Q$ where initial or non-equilibrium pressures (in atm) are used.

What is true if $Q_c = K_c$ (or $Q_p = K_p$)? Reaction at equilibrium initially

In which direction must the reaction proceed to achieve equilibrium if $Q_c > K_c$ (or if $Q_p > K_p$)?

The reaction must proceed = Reactants need to be formed to the left to achieve equilibrium = and products need to be consumed to achieve equilibrium.

In which direction must the reaction proceed to achieve equilibrium if $Q_c < K_c$ (or if $Q_p < K_p$)?

The reaction must proceed = Products need to be formed to the right to achieve equilibrium = and reactants need to be consumed to achieve equilibrium.

Lecture Concepts 9. Strategies for Calculating Equilibrium Concentrations/Pressures (and sometimes K from them)

In these types of problems, one is often given the equilibrium constant. A useful first step often is to figure out in which direction the reaction must proceed (to the left or to the right) so as to achieve equilibrium. To do this, calculate your Q.

Problem: In a reaction at 35°C, 2.0×10^{-2} mol of NO(g) is mixed in a 2.0L flask with 8.3×10^{-3} mol of Cl₂(g) and 6.8 mol of NOCl(g). If $K_c = 6.5 \times 10^4$ at 35°C, in which direction will the reaction proceed to achieve equilibrium?

$$Q_c = \frac{[NOCl]^2}{[NO]^2 \cdot [Cl]^2} = \frac{\left(\frac{6.8 \text{ mol}}{2.0 \text{ L}}\right)^2}{\left(\frac{8.3 \times 10^{-3} \text{ mol}}{2.0 \text{ L}}\right) \left(\frac{2.0 \times 10^{-2} \text{ mol}}{2.0 \text{ L}}\right)^2} = 2.8 \times 10^7$$

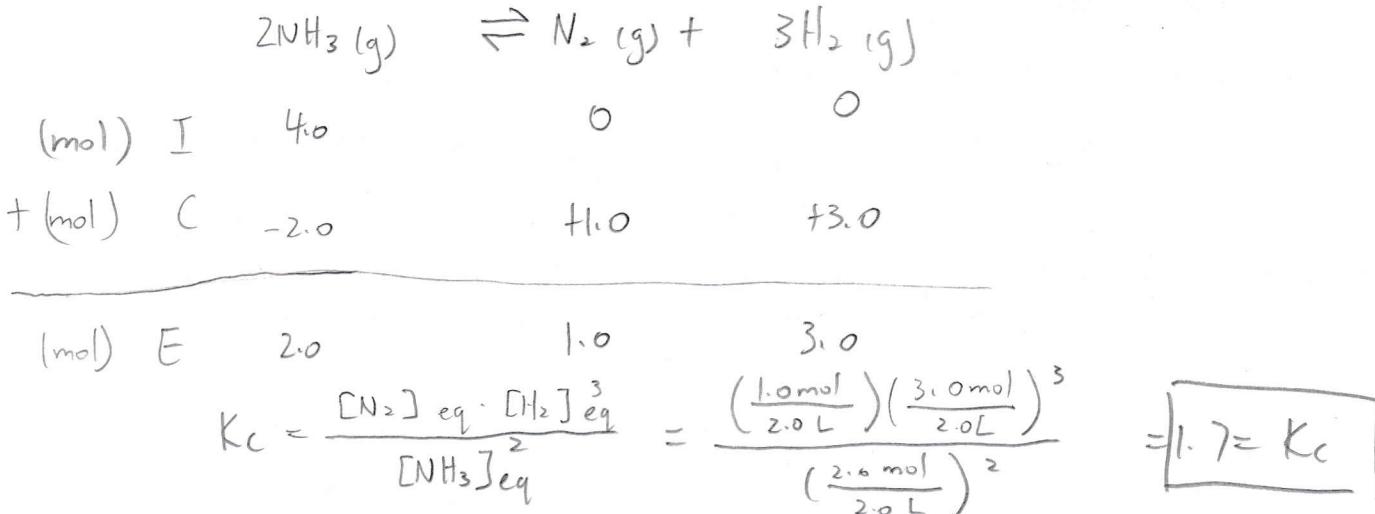
$Q_c > K_c$ Reaction proceeds to the left to achieve equilibrium.

**OK, let's get started now. When attacking problems to determine equilibrium positions, you'll never fall astray if you remember to think in terms of the following chart ↩

Remember : Ice Ice Baby → seen in the balanced equation.
(Note how the Change is based upon stoichiometry.)

Problem Type 1. (easiest) An Equilibrium Concentration is Known. At a certain temperature, 4.0 mol NH₃ is introduced into a 2.0L container and partially dissociates by the reaction:
 $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$; at equilibrium 2.0 mol NH₃ remains. What is the value of K_c?

Make your ICE chart (in moles, but could be in molarity given the constant V). Solve.



Problem type 2. (mildly harder, equilibrium and algebraic thinking). Initial concentrations known only, no equilibrium concentrations are known.

A mixture of 0.500 M $\text{H}_2(\text{g})$ and 0.500 M $\text{I}_2(\text{g})$ are placed in a 1.00 L flask at 430°C . The equilibrium constant for the written reaction is 54.3 at this temperature. Calculate the concentrations of all 3 gases at equilibrium. $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

$$K_c = 54.3$$

What's the Q here? $Q_c = 0$ since we have no problem initially (HI) $Q_c = \frac{[\text{HI}]_0^2}{[\text{H}_2]_0 [\text{I}_2]_0}$

Make your ICE chart (this time in molarity)...

	$\text{H}_2(\text{g})$	$\text{I}_2(\text{g})$	$\rightleftharpoons 2\text{HI}(\text{g})$
I	0.500	0.500	0
+ C	-X	-X	+2X
E	$0.500 - X$	$0.500 - X$	$+2X$

Set up your equilibrium expression and solve...

$$K_c = \frac{[\text{HI}]_{\text{eq}}^2}{[\text{H}_2]_{\text{eq}} \cdot [\text{I}_2]_{\text{eq}}} = 54.3 = \frac{(2X)^2}{(0.500 - X)(0.500 - X)}$$

$$\sqrt{54.3} = \sqrt{\frac{(2X)^2}{(0.500 - X)^2}} ; 7.37 = \frac{2X}{0.500 - X}$$

$$2X = [\text{HI}]_{\text{eq}} = 0.786 \text{ M}$$

$$0.500 - X = [\text{H}_2]_{\text{eq}} = [\text{I}_2]_{\text{eq}} = 0.107 \text{ M}$$

$$X = 0.393$$

Once you get your final answers, leave the exam confidently by **DOUBLE CHECKING** your answers... see that concentrations match the equilibrium constant!

$$K_c = \frac{(0.786 \text{ M})^2}{(0.107 \text{ M})^2} = 54.0$$

close enough to
54.3 for me
to be confident
of my calculations

You'll notice in this problem that there was a perfect square (be on the look-out for this or perfect cube, etc...), which simplified this problem by allowing one to take a square root. What was true about the initial concentrations that gave us the perfect square?

Don't drive yourself insane thinking: oh, is it exothermic? Endothermic? Does the temperature actually change and then the equilibrium constant. Stop worrying: if it says it's at temperature X, it's at temperature X (in a container that maintains constant temperature such as a water bath at lower temps.).

Problem Type 3. (longer) Only initial concentrations known but with no perfect square simplification. At a given temperature, for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$, the initial concentrations are 0.00623M H_2 , 0.00414M I_2 and 0.0224M HI respectively. If $K_c = 54.3$ at this temperature, calculate the concentrations at equilibrium.

- For a problem such as this, where reactants AND products are present, calculating Q is especially critical in order to know the direction of change for the ICE chart.
- Make your ICE chart and write the expression for your K.
- Rearrange your math equation in polynomial format and set equal to zero. What are you going to need to use to solve?
- Even though your equation contains a “±”, only ONE (plus or minus) will work. Which one is it in this case? (It should be common sense...)

$$Q_c = \frac{[\text{HI}]_0^2}{[\text{H}_2]_0 [\text{I}_2]_0} = \frac{(0.0224 \text{ M})^2}{(0.00623 \text{ M})(0.00414 \text{ M})} = 19.4$$

$Q_c < K_c$ Reaction proceeds to the right (products are formed) to achieve equilibrium.



$$\text{I} \quad 0.00623 \quad 0.00414 \quad 0.0224$$

(M)	$+ \text{C}$	$-x$	$-x$	$+2x$
E		$0.00623 - x$	$0.00414 - x$	$0.0224 + 2x$

$$K_c = \frac{[\text{HI}]_{\text{eq}}^2}{[\text{H}_2]_{\text{eq}} [\text{I}_2]_{\text{eq}}} = \frac{(0.0224 + 2x)^2}{(0.00623 - x)(0.00414 - x)} = 54.3$$

$$\rightarrow 54.3(0.00623 - x)(0.00414 - x) = (0.0224 + 2x)^2$$

rearrange to make a polynomial

$$\rightarrow 50.3x^2 - 0.6526x + 18.98 \times 10^{-4} = 0$$

$$\begin{cases} x_1 = 0.01141 \\ x_2 = 0.001565 \end{cases} \quad \begin{array}{l} \text{must be } \Theta \text{ since the } + \text{ gives} \\ \text{negative concentrations of } \text{H}_2 \text{ and } \text{I}_2 \end{array}$$

Once you've gotten your equilibrium concentrations... you've done a lot of math here... you're human... you make mistakes... I make mistakes... we all make mistakes... let's double-check our answer!!!

$$K_c = \frac{(0.0255 \text{ M})^2}{(0.00467 \text{ M})(0.00258 \text{ M})} = 54.0$$

close enough to (54.3)

only the last digit differs from the original

$$[\text{H}_2]_{\text{eq}} = 0.00623 \text{ M} - x = 0.00467 \text{ M}$$

$$[\text{I}_2]_{\text{eq}} = 0.00414 \text{ M} - x = 0.00258 \text{ M}$$

$$[\text{HI}]_{\text{eq}} = 0.0224 + 2x = 0.0255 \text{ M}$$

Problem Type 4. Making Your Life Easier with Less Difficult Polynomials (very small K).

Phosgene (COCl_2), a nerve gas used in World War 2, decomposes by the reaction $\text{COCl}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$ with a $K_p = 6.8 \times 10^{-9}$ at 373K. If pure phosgene with a P_i (initial pressure) = 1.0atm decomposes at this temperature, calculate the equilibrium pressures of all gases in the container. $Q=0$ since we have no products initially

Set up the ICE chart... note we can use pressures in the ICE chart (directly proportional to concentration at a given temperature). Then write the equilibrium expression...

	$\text{COCl}_2(\text{g})$	\rightleftharpoons	$\text{CO}(\text{g})$	$+ \text{Cl}_2(\text{g})$	$K_p = \frac{P_{\text{CO}} \cdot P_{\text{Cl}_2}}{P_{\text{COCl}_2}}$
(atm) I	1.0		0	0	
(atm) C	$-x$		$+x$	$+x$	$6.8 \times 10^{-9} = \frac{x \cdot x}{1.0 - x}$
(atm) E	$1.0 - x$		x	x	$1.0 - x \approx 1.0$ Approximation can be made due to having a small K value

Remember pressure is directly proportional to concentration at given temperature ($P = C \cdot R \cdot T$)

$$x = P_0 = P_{\text{Cl}_2} = 8.5 \times 10^{-5} \text{ atm}$$

$$1.0 - x = P_{\text{COCl}_2} = 1.0 \text{ atm}$$

Rather than mucking about with the quadratic equation... you know that the equilibrium constant is very small, so therefore what does this tell you about how far the reaction proceeds?

The forward reaction occurs to only a very small extent to reach equilibrium.

For very small K values, you can make the approximation that your initial reactant concentration minus nx is equal to the initial reactant concentration and that your initial product (if present) concentration plus nx is equal to the initial product concentration. Similarly, the initial reactant pressure minus nx is equal to the initial reactant pressure and that your initial product pressure plus nx is equal to the initial product pressure. The "n" is the number before the "x" in the CHANGE row of the ICE Chart.

Which inevitably leads one to the question... how small is small enough to make an approximation? The following two rules, if satisfied, allows one to make the approximation in the previous paragraph. $K_p \times 400$

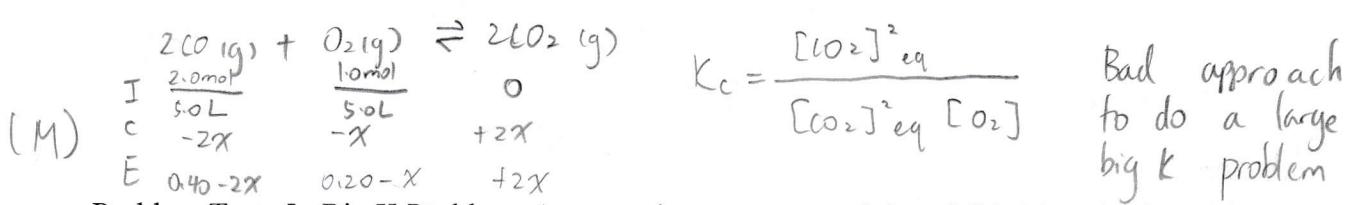
$$(6.8 \times 10^{-9}) \times 400 \ll 1 \text{ atm}$$

Numerous books show the **400x rule**. The **400x Rule** states that if the $K_c \times 400$ is less than the value of the smallest non-zero initial concentration (or if the $K_p \times 400$ is less than the smallest non-zero initial pressure), then the approximation may be made.

rule works
95% of
the time

Your book uses the **Rule of 5%**. The **rule of 5%** states that if the change "nx" is less than 5% of the initial concentration or pressure, then the approximation may be made.

Another way to see that the approximation is valid is to look at your final answers to see that the change had no effect on the initial pressures or concentrations in terms of significant figures.



Problem Type 5. Big K Problem At a certain temperature, 2.0 mol CO (g) and 1.0 mol O₂ (g) are placed in a 5.0 L vessel; calculate the equilibrium concentration of all species present given that the following reaction has a K=5.0 x 10⁵. $2\text{CO(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{CO}_2\text{(g)}$

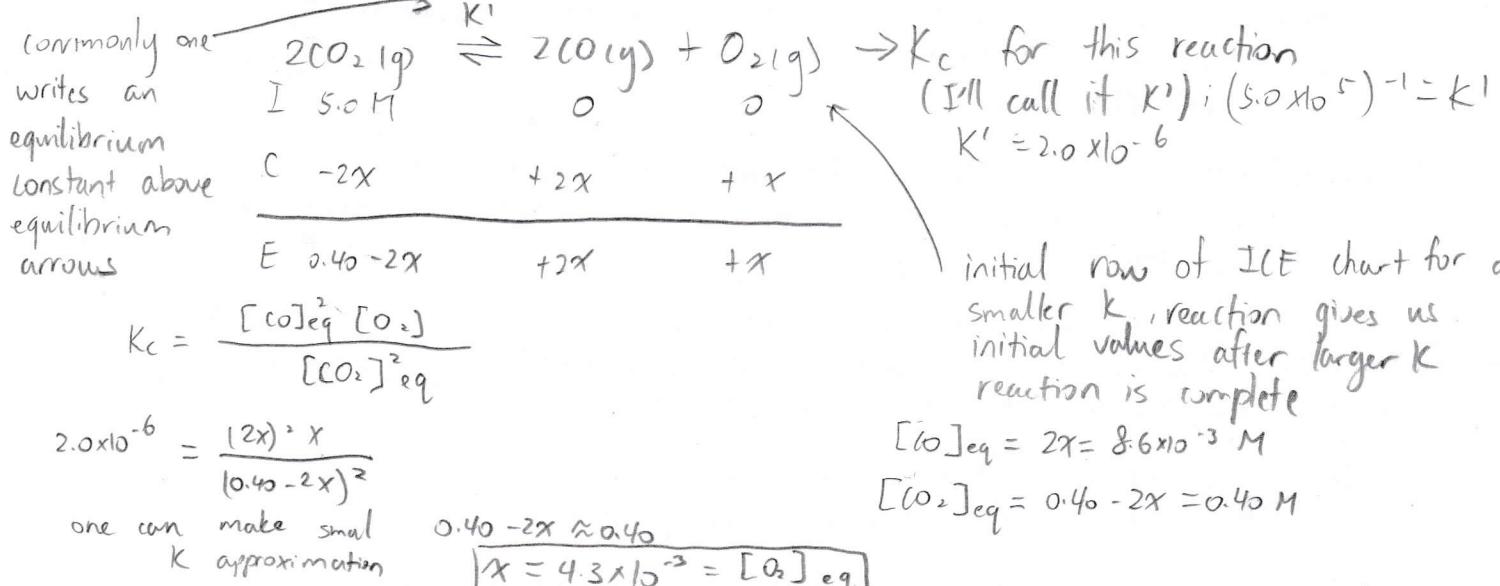
For large K problems, you may find it bizarrely unsolvable if you try to do your ICE chart in the forward direction. $(2x)^2/(0.40-2x)^2(0.20-x) = 5.0 \times 10^5$. Try this on your own if you like and prepare to be frustrated as you try to solve the problem.

So, how does one deal with a large K? Remember, a large K reaction is a reaction that has gone very close to completion. As a general rule, before doing smaller K reactions, one deals with reactions with larger K values first. So, if a reaction has a large K, one allows the reactants to be completely converted to products for these reactions (thinking about limiting reagent if need be). Only once you have brought the large K reaction to completion, then and only then may you start thinking about smaller K reactions.

Then, make an equilibrium starting with the completed large K reaction! (Make your ICE chart.) Given that it doesn't make sense that there would be 0 M CO and 0 M O₂ present at equilibrium, you can think that carbon monoxide and oxygen will be produced by the reverse reaction of the one written above; the beauty of the reverse reaction is that the reverse reaction has a small K and one can follow the rules for approximation. (Review: what is the equilibrium constant for the reverse reaction?)

If the reaction goes to completion, 2.0 mol CO reacts completely with 1.0 mol O₂ to give 2.0 mol CO₂

After taking a reaction with a large K to completion, one next does the reverse reaction.



How large does a K have to be before I start worrying that I might have a large K problem?

I look for a large K problem
when $K \geq 1000$.

Problem: Practicing With Heterogeneous Equilibria (Reminding Ourselves of Dalton's Law).

A 3.52g sample of solid ammonium carbamate, $\text{NH}_4\text{CO}_2\text{NH}_2$, is placed in an evacuated 3.80L vessel at 40°C. When equilibrium is established, the total pressure inside the vessel is 0.353 atm. What is the mass of $\text{NH}_4\text{CO}_2\text{NH}_2$ present at equilibrium? Ammonium carbamate decomposes by the equation: $\text{NH}_4\text{CO}_2\text{NH}_2(s) \rightleftharpoons 2\text{NH}_3(g) + \text{CO}_2(g)$

I	solids and	0	0
C	liquids are ignored in ICE chart	$+2x$	$+x$
E	(because solids/ liquids not part of K_c or K_p)	$2x$	x

← initially, one had
an evacuated vessel
(no gas)

Think: If we know the moles of gaseous products at equilibrium (from $PV = nRT$), one knows from stoichiometry the moles of solid that reacted as well.

At equilibrium,

$2x + x = 3x$ is
the total pressure

$3x = 0.353 \text{ atm} = \text{equilibrium pressure}$
of CO_2

$$\text{moles of } \text{CO}_2 \text{ at equilibrium} = \frac{P_{\text{CO}_2} \cdot V}{R \cdot T} = \frac{(0.1177 \text{ atm})(3.80 \text{ L})}{(0.08206 \frac{\text{atm} \cdot \text{L}}{\text{K} \cdot \text{mol}})(313 \text{ K})} = 0.0173 \text{ mol CO}_2 \text{ present at equilibrium}$$

Due to 1:1 mole ratio of $\text{NH}_4\text{CO}_2\text{NH}_2 : \text{CO}_2$ in equation,
0.0173 mol $\text{NH}_4\text{CO}_2\text{NH}_2$ reacted to reach equilibrium

$$3.52 \text{ g } \text{NH}_4\text{CO}_2\text{NH}_4 - \left(\frac{(0.0173 \text{ mol})}{\text{react}} \right) \left(\frac{78.09 \text{ g } \text{NH}_4\text{CO}_2\text{NH}_2}{\text{mol } \text{NH}_4\text{CO}_2\text{NH}_2} \right) = 2.17 \text{ g}$$

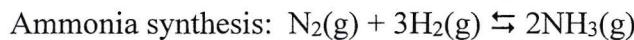
Lecture Concepts 10. Le Châtelier's Principle. Messing with a System Already at Equilibrium

Once a reaction system is at equilibrium, one might change the concentrations of reactants/products by adding/removing a reagent, one might change the pressure or alter the temperature. These effects can all be described by Le Châtelier's Principle.

What is Le Châtelier's Principle? Le Châtelier Principle states that if a change is made to a reactant at equilibrium, the system will react so as to minimize that change.

First Type of Change to System at Equilibrium. Change in Concentration.

Problem. At 720°C, the value of K_c for the reaction below showing ammonia synthesis = 2.37×10^{-3} . In an experiment, the equilibrium position is 0.683M N₂, 8.8M H₂ and 1.05M NH₃. Suppose some ammonia is added to the mixture so that the [NH₃]=3.65M.



- a) First use Le Châtelier's Principle to predict the direction of the shift to reach a new equilibrium once the ammonia is added (i.e, to the left or to the right)

The system reacts to minimize the change, so the reaction will proceed to the left to re-achieve equilibrium after the NH₃ is added.

- b) Now confirm the Le Châtelier's Principle prediction by calculating the Q_c for the initial concentrations once the ammonia is added and comparing with K_c.

$$Q_c = \frac{[NH_3]_{eq}^2}{[N_2]_{non-eq}[H_2]_{non-eq}^3} = \frac{(3.65\text{ M})^2}{(0.683\text{ M})(8.8\text{ M})^3} = 0.029 \quad Q_c > K_c$$

[A]_{non-eq} = non-equilibrium concentration of A (in M)

Effect of a Change of Pressure on a System at Equilibrium

∴ reaction shifts
left to achieve
equilibrium

There are three types of changes one could make to your system that would result in a change of pressure, that you should consider separately. List them below.

1. adding or removing a gaseous reactant or product.
2. adding an inert gas (inert = unreactive)
3. increasing or decreasing the volume of the reaction container

Let's consider the reaction $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ as a template reaction. (for the rest of the page)

Scenario 1. Adding gaseous reactants/products. Your pressure goes up, your concentration goes up in the volume of your container. Treat the same as concentrations for determination of the direction of shift to re-achieve equilibrium. Let's see if you've got it. For the template reaction imagine some NO_2 is removed from the system; which way will the system shift to re-achieve equilibrium? The system will shift to the left to create more $\text{NO}_2(\text{g})$, to minimize the change.

Scenario 2. Adding an inert gas. Think of some classic unreactive gases.

The noble gases. From Dalton's Law of Partial pressures, the partial pressure of one gas is NOT affected by the partial pressure of a second gas.

Let's imagine you increase the pressure by adding one of these gases to the above reaction system. What happens to the relative concentrations of reactants and products?

$$\underbrace{P_{\text{NO}_2} + P_{\text{N}_2\text{O}_4}}_{\substack{\text{pressures at} \\ \text{equilibrium}}} + P_{\text{inert gas}} = P_{\text{total}}$$

$$K_p = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2}$$

↳ adding an inert gas causes no change to the concentrations of reactants & products

So, what direction will the reaction "shift to re-achieve equilibrium"?

In no direction, the reaction is still at equilibrium after adding the inert gas.

Scenario 3. Changing the volume of the container. Let's say, for the reaction $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ at equilibrium, we all of a sudden decrease the volume of the container by half. What happens to the concentration of our gases?

Right after decreasing the volume by half, the concentrations of the gas will double.

Let's say the equilibrium concentrations were $x \text{ M}$ for NO_2 and $y \text{ M}$ for N_2O_4 . What would the equilibrium constant K then be?

$$K_c = \frac{[\text{N}_2\text{O}_4]_{\text{eq}}}{[\text{NO}_2]^2_{\text{eq}}} = \frac{y}{x^2}$$

After decreasing the volume of the container by half, what would the value of Q be?

→ immediately after decreasing volume of container

$$Q_c = \frac{[\text{N}_2\text{O}_4]_{\text{non-eq}}}{[\text{NO}_2]^2_{\text{non-eq}}} = \frac{2y}{(Rx)^2} = \frac{y}{2x^2}$$

To which side, if any, would the reaction shift to re-achieve equilibrium?

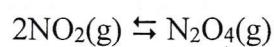
Since $Q_c < K_c$, reaction shifts to the right to achieve equilibrium after decreasing volume. So, as a general rule, if one increases the pressure by decreasing the volume of the container, the reaction will shift to the side with of chemical equation with fewer moles of gases to re-achieve equilibrium. If one decreases the pressure by increasing the volume of the container, the reaction will shift to side with of chemical equation with more moles of gases

Note: The equilibrium constant did NOT change upon a change of pressure or concentration!

However, K does change with temperature.

The Effect of a Change in Temperature on a Reaction at Equilibrium

Let's consider our reaction:



← A bond is forming as this
reaction occurs
As a consequence
 $\Delta H = \text{negative}$

(Review: What's happening to ΔH for this reaction?)

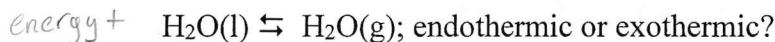
I find it helpful to write the energy on the side of the reaction as appropriate.

- **Endothermic** means you're putting energy into the system, so treat **energy as a reactant** in this case.
- **Exothermic** means energy is released from the reaction as heat, so treat **energy as a product** in this case.

Then, as you raise the temperature you're increasing this "energy". So if the temperature is raised, in which direction will the reaction shift to re-achieve equilibrium for $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$? *Reaction shifts → left (to minimize change that resulted in an increase of "product" "energy") to re-achieve equilibrium.*

An endothermic reaction will shift to the right upon increasing temperature and will shift to the left upon decreasing temperature. An exothermic reaction will shift to the left upon increasing temperature and will shift to the right upon decreasing temperature. Since the effect of temperature on the system at equilibrium is directly related to exothermicity or endothermicity, it's useful to think of exothermic and endothermic reactions you know.

Let's consider how you boiled your water for your morning tea/coffee/tisane:



For $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$, which direction is favoured as the temperature is increased?

Increasing temperature results in a shifting of this reaction to the right.

Rather than thinking there's something mysterious about the effect of increasing temperature on the equilibrium system for a reaction, often logic prevails. In an example like $\text{F}_2(\text{g}) \rightleftharpoons 2\text{F}(\text{g})$, what you're doing is breaking a bond; do you think breaking a bond is more favoured at higher or at lower temperatures? *energy + $\text{F}_2(\text{g}) \rightleftharpoons 2\text{F}(\text{g})$*

↳ Bond-breaking is favoured at higher temperatures

What we'll see in fact, is that K itself increases for an endothermic reaction (decreases for exothermic reaction) with an increase in temperature, something we'll get a mathematical sense for in an upcoming section.

Chapter 14

Zumdahl Textbook

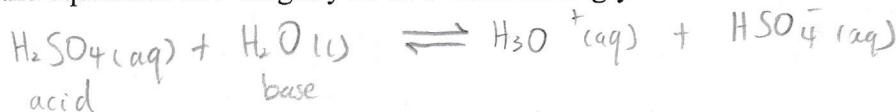
Lecture Concepts 11. Applying Equilibrium Constants to (Aqueous) Solution Chemistry 1. The Vocabulary of the Equilibrium of Acid-Base Reactions

Let's remind ourselves of some definitions from the previous course:

Brønsted-Lowry Acid: H⁺ donor

Brønsted-Lowry Base: H⁺ acceptor

Show the reaction between water and H₂SO₄ and label the acid and the base; in which direction does the equilibria lie? Slightly so or overwhelmingly so? This reaction has an immeasurably large k.



Equilibrium lies overwhelmingly to the right ($\text{H}_3\text{O}^+(\text{aq})$ and $\text{HSO}_4^-(\text{aq})$ are present

$\text{H}_3\text{O}^+(\text{aq})$ is called the hydronium ion and is sometimes written as:

The $\text{H}_3\text{O}^+(\text{aq})$ ion is the conjugate acid of water.

Define the above term. The conjugate acid of a substance is the species that is formed when that substance accepts a single H⁺.

$\text{HSO}_4^-(\text{aq})$ is the conjugate base of $\text{H}_2\text{SO}_4(\text{aq})$.

Define the above term. The conjugate base of a substance is the species that is formed when that substance loses a single H⁺.

Define a conjugate acid-base pair. = CA - CB pair

two substances that differ by a single H⁺

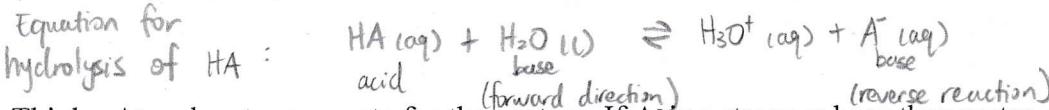
substance reacts with H₂O in a hydrolysis.

Are H₂SO₄ and SO₄²⁻ a conjugate acid-base pair?

No, since they differ by two H⁺

Write the hydrolysis equation for a generic acid HA below (with equilibrium arrows).

(vocabulary: hydrolysis for acid = acid dissociation in water)

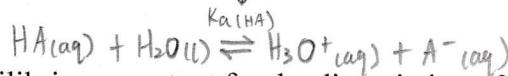


Think: A⁻ and water compete for the proton. If A⁻ is a stronger base than water, the equilibrium will lie toward which side? left (since HA will be made) If water is a stronger base than A⁻, which side will the equilibrium lie toward?

Right (since H₂O(l) being a stronger base will more successfully get the H⁺ making $\text{H}_3\text{O}^+(\text{aq})$).

(from previous page)

One commonly writes equilibrium constant
for a reaction above arrows



The equilibrium constant for the dissociation of acid has a special name: the **acid dissociation constant** (acid dissociation constant = K_a). Write this equilibrium constant below.

$$K_a = \frac{[\text{H}_3\text{O}^+]_{\text{eq}} [\text{A}^-]_{\text{eq}}}{[\text{HA}]_{\text{eq}}}$$

Do you think that an acid is more or less acidic the larger the acid dissociation constant?

An acid is more acidic and an acid is stronger
the larger the K_a value

- Remember what acid strength means:

The stronger an acid HX(aq) , the more that acid
is dissociated into $\text{H}_3\text{O}^+(\text{aq})$ and $\text{X}^-(\text{aq})$

List the 6 common strong acids here (there are other strong acids, but THESE are the ones you should know by heart). If you see another strong acid, you will be told it's strong. Other acids, chances are, will be weak (and will typically be given with a small K_a value).

6 common strong acids

- ① HCl(aq)
- ② $\text{HNO}_3(\text{aq})$
- ③ $\text{H}_2\text{SO}_4(\text{aq})$
- ④ HBr(aq)
- ⑤ HI(aq)
- ⑥ $\text{HClO}_4(\text{aq})$

These acids are completely dissociated
into $\text{H}_3\text{O}^+(\text{aq})$ and $\text{X}^-(\text{aq})$.

What makes these strong acids (thinking in terms of equilibrium)?

These acids have a large K_a value when
placed in H_2O large $K_a = K_a \gg 1$

What is true about weak acids (in terms of equilibrium)?

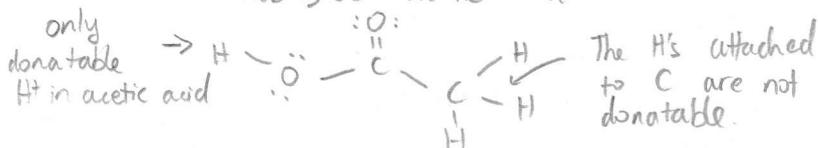
Weak acids have a small K_a value when
placed in H_2O small $K_a = K_a \ll 1$

Many acids are oxyacids. To what atom is the H typically bound for oxyacids?

Oxyacids = acid containing oxygen
(Draw the Lewis structures of nitric acid, acetic acid.)

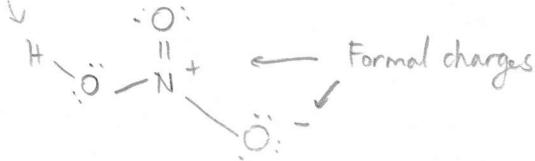
The monoprotic acid

$\text{HC}_2\text{H}_3\text{O}_2$ = acetic acid



donatable H^+

acidic H is attached (typically) to oxygen.



What is meant by an amphoteric substance?

a substance is amphoteric if it can
act as either an acid or as a base in H_2O .

Write an example of an amphoteric substance.

amphoteric substances: $\text{HCO}_3^-(\text{aq})$ = bicarbonate, $\text{HSO}_3^-(\text{aq})$ ← substances that I don't tell you are amphoteric, assume that they are not amphoteric



Water is also amphoteric, and the reaction of one molecule of water with a second molecule of water is what is known as the **autoionization** of water. **Autoionization** is the reaction where one molecule of a given substance acts as a Brønsted-Lowry Acid and the second molecule of that same substance acts as a Brønsted-Lowry base.

autoionization of water:



The autoionization equilibrium for water (since water is such an important chemical) has a specially named equilibrium constant, called the **ion-product constant**. (**ion product constant = dissociation constant for water = K_w**). Write the mathematical equation for K_w and then give the value for this constant at 298K.

$$K_w = [\text{H}_3\text{O}^+]_{\text{eq}} [\text{OH}^-]_{\text{eq}}$$

$$\text{At } 298\text{ K, } K_w = 1.0 \times 10^{-14} \quad \leftarrow \text{memorize this value}$$

So, the product of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ at 25°C will always be 1.0×10^{-14} . However, do note that the autoionization of water is endothermic, so K_w increases with temperature.

Autoionization is reverse of reaction between $\text{H}_3\text{O}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$
If the $[\text{H}_3\text{O}^+] > [\text{OH}^-]$, what does this say about the solution? Solution is acidic

What if $[\text{H}_3\text{O}^+] < [\text{OH}^-]$? Solution is basic

If $[\text{H}_3\text{O}^+] = [\text{OH}^-]$? Solution is neutral

Problem: If an aqueous solution is 1.0×10^{-5} M in OH^- , what is the concentration of H^+ ? Is the solution acidic or basic? (To note: There might be other solutes in the aqueous solution. Note: You should assume the temperature is 298K if not given other information.)

Brønsted Lowry Acid-Basic reactions take place instantaneously,

You can assume that 1.0×10^{-5} M OH^- is an equilibrium concentration.

$$K_w = [\text{H}_3\text{O}^+]_{\text{eq}} [\text{OH}^-]_{\text{eq}}$$

$$1.0 \times 10^{-14} = [\text{H}_3\text{O}^+]_{\text{eq}} \cdot (1.0 \times 10^{-5} \text{ M})$$

$$[\text{H}_3\text{O}^+]_{\text{eq}} = [\text{H}^+]_{\text{eq}} = 1.0 \times 10^{-9} \text{ M}$$

since $[\text{OH}^-]_{\text{eq}} > [\text{H}^+]_{\text{eq}}$ ∴ solution is basic

The pH scale

Since concentrations of $[H^+]$, $[OH^-]$ and other solutes may be very small in aqueous solution, it is often useful to express them in terms of a logarithm.

When you see lower-case p followed by something... what does it mean? $-\log(\text{something})$

$$pH = -\log [H_3O^+]_{eq} \quad pOH = -\log [OH^-]_{eq} \quad pCl = -\log [Cl^-]_{eq} \quad pK_a = -\log K_a$$

Students for some reason tend to get mixed up with the meaning of your pX values. Let's try to make sure YOU don't... $K_a = \frac{[H^+][A^-]}{[HA]}$

As the pK_a increases, what is happening to the strength of the acid? (Increasing or decreasing)

As pK_a increases for an acid, the K_a decreases, the strength of the acid decreases.

As your pH goes up, is your solution becoming MORE or LESS basic?

As pH goes up, $[H^+]$ goes down and the solution becomes less acidic and more basic

Problem: Let's say you have an $[OH^-] = 6.7 \times 10^{-12}$ M, what is the pOH ? (sig figs!)

1) is not considered significant since it does not tell about precision.
1) only tells me $[OH^-]$ between 10^{-11} and 10^{-12}

$pOH = -\log(6.7 \times 10^{-12}) = 11.18$ ← correct answer in terms of sig figs
 when talking about a number obtained from a logarithm only the numbers after decimal are significant.

Problem: Remember that for any pX scale, since pX is a logarithmic scale, that a change of 1 pX equals a 10-fold change in X. Illustrate this with the following pK_a s (note some of the math too if you're rusty on logarithmic mathematics), by converting them back to K_a s.

$$\begin{array}{lll} pK_a = 6.5 & \begin{matrix} \checkmark \\ 1 \text{ sig fig} \end{matrix} & -\log K_a = 6.5 \\ & -\log K_a = 6.5 & 10^{-(1-\log K_a)} = 10^{-(pK_a)} = 10^{-6.5} = K_a = \boxed{3 \times 10^{-7}} \\ pK_a = 5.5 & \begin{matrix} \checkmark \\ 1 \text{ sig fig} \end{matrix} & -\log K_a = 5.5 \\ & -\log K_a = 5.5 & 10^{-5.5} = K_a = \boxed{3 \times 10^{-6}} \end{array}$$

In an experiment, a pH meter is the device that measures the pH of a solution. *How does a pH meter work? A probe containing aqueous acidic solution has a different pH than the solution being tested. An electric potential results, and then pH may be read on a digital display.*

We're going to derive now a useful equation in pH problems.

$$\text{As we know, } K_w = [\text{H}^+][\text{OH}^-]$$

Take the $-\log$ of both sides of the equation above.

$$-\log K_w = -\log ([\text{H}^+]_{\text{eq}} [\text{OH}^-]_{\text{eq}})$$

What is $\log(A \cdot B) = ?$ Then apply this equation to the above equation and then set in pX form.

$$[\log A + \log B] - \log K_w = pK_w = -\log [\text{H}^+]_{\text{eq}} - \log [\text{OH}^-]_{\text{eq}}$$

If we're at 298K (one is often close in lab), what is the $pK_w = ?$

At 298K

$$K_w = 1.0 \times 10^{-14}; pK_w = -\log K_w = 14.00$$

This then gives us the final equation in pX form as...

At 298K

$$14.00 = \text{pH} + \text{pOH}$$

For a neutral solution, $[\text{H}^+] = [\text{OH}^-]$

$$\therefore \text{pH} = \text{pOH} \quad \text{pH} = 7.00 \text{ for this solution}$$

Problem: The pH of a fruit juice is 5.5. Calculate the pOH and $[\text{OH}^-]$.

$$14.00 = 5.5 + \text{pOH}$$

$$\text{pOH} = 8.5$$

$$10^{-\text{pOH}} = [\text{OH}^-] = 3 \cdot 10^{-9}$$

\downarrow
1 sig fig

In the next sections, you will be asked to determine the pH/pOH and equilibrium concentrations of other species for a variety of solutions including strong acids, strong bases, weak acids, weak bases, mixtures of acids, salts, mixtures of acids and salts, mixtures of bases and salts. To succeed with these problems, you always need to think what is/are my **MAJOR SPECIES** for a solution. You will **only consider reactions involving major species** when calculating the equilibrium concentrations of the solution.

Water, remember, is a **major species** in ALL aqueous solutions. Strong acids HX(aq) exist not intact, but are completely dissociated into H^+ (aq) and X^- (aq) as major species. Soluble ionic compounds exist completely dissociated into the cations and anions that make them up. Weak acids HX(aq) exist as a major species in undissociated HX(aq) form. Weak bases and slightly soluble salts exist in undissociated form. (Review solubility rules if need be.)

You can think that the major species are all species present in a solution created by a large K reaction. (Large K reaction = reaction that goes to completion.) If setting up an ICE chart associated with a small K reaction, one puts the value (for example, concentration) for each reactant and product in the "I" row that corresponds to the value present assuming all larger K reactions have already occurred.

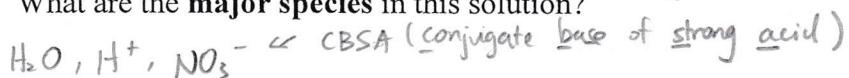
Lecture Concepts 12. Applying Equilibrium Constants to (Aqueous) Solution Chemistry 2.
Calculating the pH of Strong and Weak Acid Solutions. Percent Ionization.

Template 1. Strong Acid Dissolved in Water

Problem: Calculate the pH of HNO_3 (0.1M) at 25°C (Note: assume aqueous! Note: listed molarity of solutes means "molarity, not having yet considered any dissociation".)

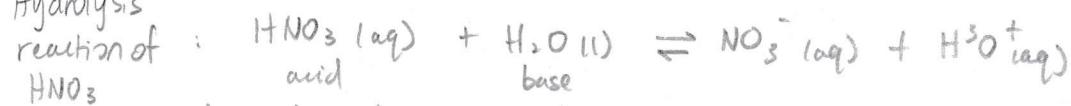
Thought process: 1. Nitric acid: strong acid or weak acid?

2. What are the **major species** in this solution?



In this problem, the anion is a **conjugate base of a strong acid**. (Conjugate base of strong acid = CBSA.) A CBSA has no effect on the pH since a CBSA does not react with H^+ or OH^- to any significant degree. Cross out the CBSA as an irrelevant **major species** above for what is critical here, **determining the pH** of this solution. Show why the CBSA does not react with H^+ below.

Hydrolysis



Forward reaction has a very large K.

∴ Reverse reaction has a very small K ∵ NO_3^- does not react with H^+ to any significant degree

Now you need to think here, and what we're always interested in, what are the major species dictating our pH? If the concentration of strong acid solute is $\sim 1.0 \times 10^{-5}$ M or greater, ignore the impact of water on the pH and focus on the $[\text{H}^+]$ produced from the strong acid dissociating. (Now solve the problem, thinking about sig figs.)

0.1 M HNO_3 dissociates completely into 0.1 M H_3O^+ and 0.1 M NO_3^-

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.1) = 1.0 = \text{pH}$$

\uparrow
1 sig fig

Problem: Determine the pH of 1.0×10^{-10} M HBr at 25°C.

✓ CBSA does not affect the pH of the solution

Major species: $\text{H}^+, \text{Br}^-, \text{H}_2\text{O}$

Cross out any major species that are irrelevant to pH determination.

If the concentration of an acid or base solute is 1.0×10^{-9} M or less, since the solute is so dilute, water dictates the pH and pure water has a pH of 7.00.

↑

$$\text{pH} = 7.00 \text{ for } 1.0 \times 10^{-10} \text{ M HBr}$$

Now, all this is fine and well, sir, but WHY should we CARE how to predict pH from calculation? Reactions are pH sensitive, biological samples need to be stored at certain pH values.

Calculating the pH of a Weak Acid Solution

small value of K_a
means HNO_2 is a
weak acid

Problem: Calculate the pH of a 0.36M HNO_2 solution ($K_a(\text{HNO}_2)$: 4.0×10^{-4}). (assume 298K)

As always, write out the major species.



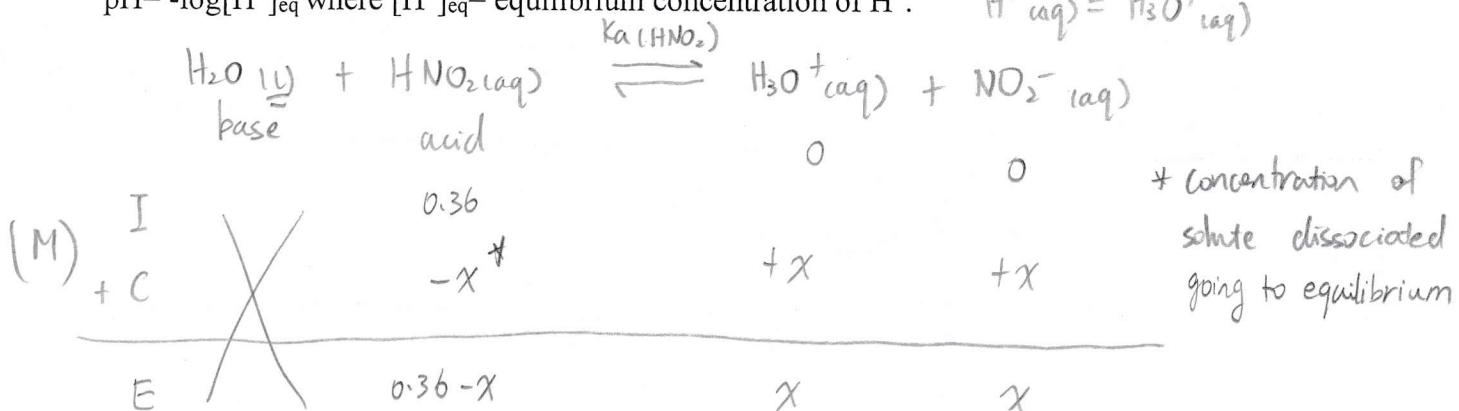
Given that the concentration of nitrous acid is fairly high ($>> 1.0 \times 10^{-7}$ M of H^+ contribution in neutral water) and that the $K_a(\text{HNO}_2) >> K_w$, one will assume that the weak acid solute dictates the pH. (What would one do if the K_a were not given for a book problem?)

K_a values are found in appendix of Zumdahl

*In fact, for your purposes in an exam, there will be no problem where you will have a weak acid (or a weak base) and water, where BOTH weak acid & water will be making a contribution to the pH. (How one deals with situations where both water & weak acid influence the pH is NOT an intuitive calculation and is taught in advanced analytical chemistry courses. The actual general rule (when you get more advanced) is that, if the $[\text{H}^+]^2$ that one calculates assuming the impact on the $[\text{H}^+]$ by water is negligible is more than 100-fold greater than K_w , the impact of water on the pH is treated as negligible.) For most every practice or exam problem on weak acids (or weak bases) I've seen at the General Chemistry level, the impact of water on the pH is negligible, and it is the solute weak acid (or bases) that dictates the pH.

Let's proceed... 0.36M HNO_2 . We've determined that HNO_2 is the major species that will dictate the concentration of H^+ in solution. So, it, being a weak acid, produces H^+ via dissociation.

Write out your ICE chart, make a mathematical equation for the K_a from it. Then, solve for the pH. Keep in mind that since Bronsted-Lowry acid-base reactions occur quickly, that the value of $\text{pH} = -\log[\text{H}^+]_{\text{eq}}$ where $[\text{H}^+]_{\text{eq}} = \text{equilibrium concentration of H}^+$.



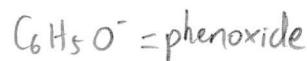
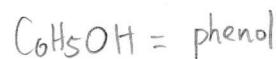
$$K_a(\text{HNO}_2) = \frac{[\text{H}_3\text{O}^+]_{\text{eq}} [\text{NO}_2^-]_{\text{eq}}}{[\text{HNO}_2]_{\text{eq}}}$$

$$4.0 \times 10^{-4} = \frac{(X)(X)}{(0.36 - X)} - \frac{X^2}{0.36}$$

Small K approximation $0.36 - X \approx 0.36$

$$X = 0.012 = [\text{H}_3\text{O}^+]_{\text{eq}}$$

$$\text{pH} = -\log X = 1.92 = \boxed{\text{pH}}$$



Calculating the pH when a Mixture of Weak Acids are Dissolved in Water

Mix of
2 weak
acids

Problem: Calculate the pH of an aqueous solution of 1.0 M HF and 1.0M C₆H₅OH. Then calculate the concentration of C₆H₅O⁻ (in M) present at equilibrium. (K_a(HF): 7.2 x 10⁻⁴; K_a(C₆H₅OH): 1.6 x 10⁻¹⁰).

Write out the major species:



Let's see if you've got it. Which of these major species dictates the pH (i.e., which of these major species is the dominant producer of H⁺?). Set up the appropriate equation to show how H⁺ is produced from the dominant H⁺-producing major species. Solve.

HF is dominant producer of H⁺ since K_a(HF) > K_a(C₆H₅OH), K_w

				K _a (HF)	
					Do reaction with larger K value before reaction with smaller K
(M)	I	1.0		0	
	+ C	-x	+x	+x	
	E	1.0-x	x	x	

$$K_a(\text{HF}) = \frac{[\text{H}_3\text{O}^+]_{\text{eq}} [\text{F}^-]_{\text{eq}}}{[\text{HF}]_{\text{eq}}} \Leftrightarrow 7.2 \times 10^{-4} = \frac{x \cdot x}{1.0-x} = \frac{x^2}{1.0} \Rightarrow x = 0.027 = [\text{H}_3\text{O}^+]_{\text{eq}}$$

small K approximation: $1.0-x \approx 1.0$ less than 5%.

Now, what about the concentration of C₆H₅O⁻? There's only one reaction by which this species is produced. Write the reaction. Remember that the initial hydronium ion in your ICE Chart for this reaction is that created from the larger K reaction, the dissociation of HF (as always, consider that the larger K reactions have already occurred before the smaller K reactions).

				phenol	
					Initial molarities are
(M)	I	1.0			molarities after larger K
	+ C	-x	+x	+x	reaction is complete.
	E	1.0-x	x	0.027+x	

$$K_a(\text{phenol}) = \frac{[\text{C}_6\text{H}_5\text{O}^-]_{\text{eq}} [\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{C}_6\text{H}_5\text{OH}]_{\text{eq}}}$$

$$1.6 \times 10^{-10} = \frac{x(0.027+x)}{(1.0-x)} = \frac{x(0.027)}{1.0} \Rightarrow x = \boxed{5.9 \times 10^{-9} \text{ M} = [\text{C}_6\text{H}_5\text{O}^-]}$$

Note how the impact on the H⁺ concentration by the C₆H₅OH species is indeed negligible.

Percent Dissociation (or Ionization) of Weak Acid (or Weak Base) Solutions

Percent dissociation = percent ionization = $\frac{\text{concentration of solute dissociated}}{\text{initial concentration of solute}} \times 100$

units must be same → in numerator and denominator

For example, we saw earlier that 0.36 M HNO₂ produced 0.012 M H⁺ or NO₂⁻; so what consequently is the % dissociation?

$$\% \text{ dissociation} = \frac{[\text{H}^+]_{\text{aq}}}{[\text{HNO}_2]_0} \times 100 = \frac{0.012 \text{ M}}{0.36 \text{ M}} \times 100 = 3.3\%$$

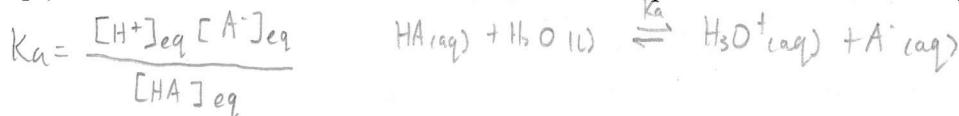
If you do an equivalent calculation with K_a, you'll see that 3.6M HNO₂ however produces 0.038M H⁺, or if you prefer, you could say that 0.038M of HNO₂ has dissociated if you consider the 1:1 stoichiometry. What is the % ionization in this case?

$$\% \text{ dissociation} = \frac{0.038 \text{ M}}{3.6 \text{ M}} = 1.1\%$$

From this example, what can you observe appears to happen to the % dissociation as a weak acid (weak base) solution becomes more dilute?

The % dissociation increases as weak acids gets more dilute.

To help you think about this, write the mathematical expression for the K_a of a generic acid HA.



Now imagine, at a given moment, that water were added and all aqueous species were suddenly diluted 10-fold. In what direction must the hydrolysis (K_a, acid dissociation) reaction shift to re-achieve equilibrium?

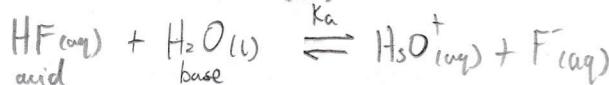
Immediately after diluting solution with acid at equilibrium 10-fold; what is Q?

$$Q = \frac{([\text{H}^+]_{\text{non-eq}})([\text{A}^-]_{\text{non-eq}})}{[\text{HA}]_{\text{non-eq}}} = \frac{(\frac{1}{10}[\text{H}^+]_{\text{eq}})(\frac{1}{10}[\text{A}^-]_{\text{eq}})}{(\frac{1}{10}[\text{HA}]_{\text{eq}})}$$

since Q < K, react shifts right to reach equilibrium

Problem: The percent dissociation is 8.1% in a 0.100M solution of HF. Calculate the K_a.

$$\frac{8.1}{100} = \frac{\% \text{ dissociation}}{100} = \frac{\text{concentration of HF dissociated}}{\text{initial concentration of solute (HF)}} = \frac{x}{0.100 \text{ M}} = x = 8.1 \times 10^{-3}$$



(M)	I	0.100	X	0	0
	C	-X		+X	+X

$$K_a = \frac{x^2}{0.100 - x} = \frac{(8.1 \times 10^{-3} \text{ M})^2}{(0.100 - 8.1 \times 10^{-3} \text{ M})} = 7.1 \times 10^{-4}$$

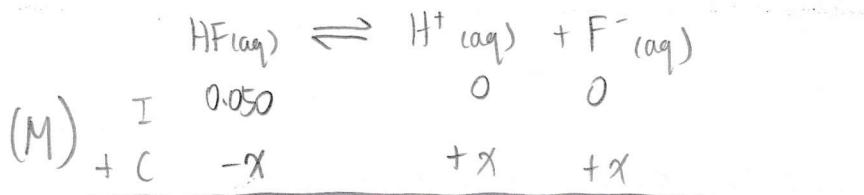
// stop point for midterm //

(Not responsible for this method)

For your own knowledge: Method of Successive Approximations. (An alternate technique (too long to be examinable) if approximations aren't valid)

Problem: Calculate the pH of a 0.050M HF solution @ 25°C ($K_a(\text{HF})$: 7.2×10^{-4})

First, solve as if making a small K approximation were valid...



$$K_a(\text{HF}) = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{x \cdot x}{0.050 - x} = \frac{x^2}{0.050 - x} = \frac{x^2}{0.050} = x^2 / 0.050$$

$x = 6.0 \times 10^{-3}$ ← Bad small k approximation

We see that the approximation is not valid, so make a polynomial equal to zero that results from the Law of Mass Action equation. If we use the method of successive approximations, one plugs in the approximated answer above for all "x"s but one and solves for "x"

$$7.2 \times 10^{-4} = \frac{x^2}{(0.050 - x)}$$

} Law of Mass Action Equation

Rearrange to get polynomial = zero

$$x^2 + (7.2 \times 10^{-4})x - (3.6 \times 10^{-5}) = 0$$

$$x^2 + (7.2 \times 10^{-4})(6.0 \times 10^{-3}) - (3.6 \times 10^{-5}) = 0$$

$$x = 5.6 \times 10^{-3}$$

In the prior step, a new value for "x" is obtained. Now, plug this new value into the equation, substituting for all "x"s but one. Solve for "x" again

$$x^2 + (7.2 \times 10^{-4})(5.6 \times 10^{-3}) - 3.6 \times 10^{-5} = 0$$

$$x = 5.6 \times 10^{-3}$$

Since both "x"s are equal to 5.6×10^{-3} , 5.6×10^{-3} M is correct "x".

$$\text{pH} = -\log x = 2.25$$

Repeat the above step until your value of "x" is the same as the value substituted for all "x"s but one. Once the underlined part of the previous sentence is true, you have reached the correct value for "x".

This technique, called the method of successive approximations, would not be on an exam, as it is too time-consuming an approach to be testable, but sometimes this method is the only way to solve an equilibrium problem. (For the problem above, you could have used the quadratic equation instead.)

With method of successive approximations, make an educated guess as to the value of "x".

One trick is to find "x" assuming the small k approx. is valid (it isn't).

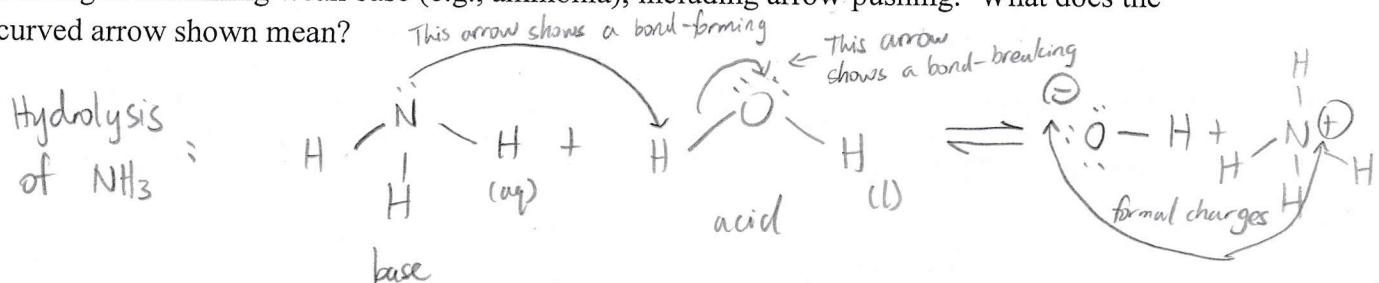
Lecture Concepts 13. Applying Equilibrium Constants to (Aqueous) Solution Chemistry 3.
Calculating the pH of Weak Base, Polyprotic Acid Solutions.

Group IA alkali metal hydroxides (MOH) and group IIA alkaline earth metal hydroxides (M(OH)_2) are said to be strong bases ($\text{M}=\text{metal}$). Note that alkaline earth metal hydroxides are moderately soluble: for example, Ba(OH)_2 is soluble up to around 0.010 M. The $\text{OH}^-(\text{aq})$ ion produced when these bases dissolve reacts completely with all acids, weak or strong. Due to the complete reaction in the previous sentence, $\text{OH}^-(\text{aq})$ is said to be a strong base. $\hookrightarrow \text{OH}^-(\text{aq})$ is the

Define **weak base**.

B=base
 (best H^+ acceptor)
 in $\text{H}_2\text{O}_{\text{lit}}$

Note that many weak bases do not have OH in their structure. One very common type of weak base is a nitrogen containing compound such that the N bears lone pairs. Show the hydrolysis of a nitrogen containing weak base (e.g., ammonia), including arrow-pushing. What does the curved arrow shown mean?



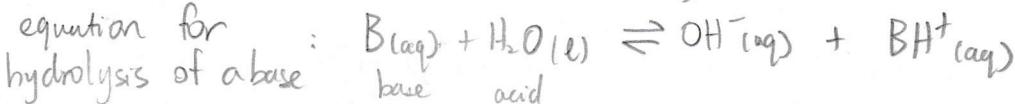
curved arrow \leftarrow The use of curved arrows to show bond-forming and bond-breaking is called arrow pushing

where a pair of electrons start \curvearrowright where a pair of e⁻'s end

The equilibrium constant that governs the dissociation (dissociation = hydrolysis) of a base in water is called the K_b . Write a generic chemical equation for the hydrolysis, then write the mathematical equation for this constant below, using B as a generic term for a base.

General chemical

K_b (of B)



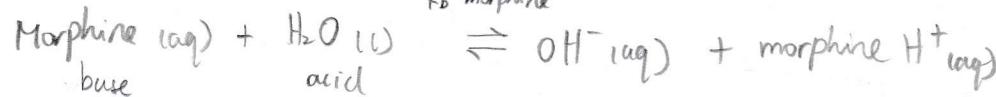
Note in the equilibrium that the base B is competing with OH^- for a proton. Since $\text{OH}^-(\text{aq})$ is the strongest base in water, the K_b value consequently is small. (vocabulary: strongest base in water = best Brønsted-Lowry base in water = most effective species possible at accepting H^+ in water)

(Practicing with Weak Bases) Problem: Morphine is a naturally occurring alkaloid often used to reduce pain for terminally ill patients in hospice. What is the pH of a 0.0075M solution of morphine at 25°C? (K_b (morphine): 1.6×10^{-6} @ 25°C)

major species: morphine, H₂O
What major species are present? Which major species would you predict is dictating the pOH (and therefore the pH)? Set up your equilibrium expression and solve.

K_b (morphine) $\gg K_w$ ∴ morphine dictates the [OH⁻] and ∵ the [H⁺]

K_b morphine



$$-\log x = pOH = 3.96$$

$$\uparrow 14.00 - pOH = 3.96$$

$$x = 1.1 \times 10^{-4}$$

$$[\text{OH}^-] = x$$

$$K_b = \frac{[\text{morphine H}^+]_{\text{eq}} [\text{OH}^-]_{\text{eq}}}{[\text{morphine}]_{\text{eq}}} ; 1.6 \times 10^{-6} = \frac{x^2}{0.0075 - x} = \frac{x^2}{0.0075}$$

$$\text{small } K \text{ approximation: } 0.0075 - x \approx 0.0075$$

Dealing with Polyprotic Acids

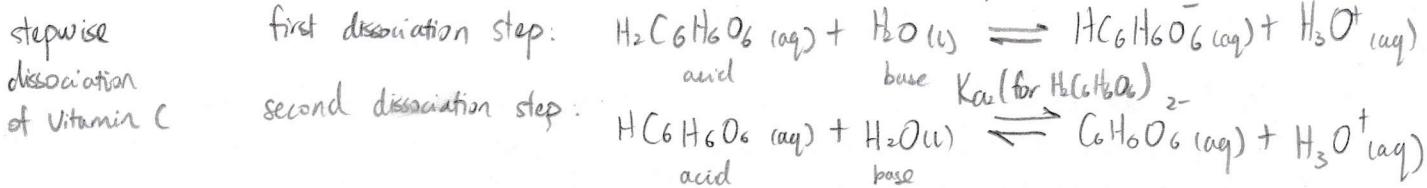
Define polyprotic acid.

A substance that can donate more than one H⁺ to H₂O

Based on calculations agreeing with experimental data, it's useful to think of polyprotic acids as dissociating in a stepwise fashion. Show as an example the stepwise dissociation of diprotic acid

Vitamin C as an example (H₂C₆H₆O₆(aq)).

K_{a_1} (for H₂C₆H₆O₆)



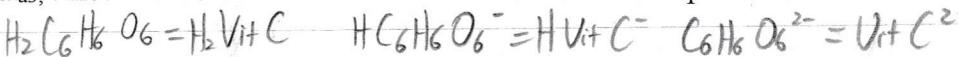
Note: not all H⁺ in Vitamin C gets donated to water. Why? Some of the hydrogens are bonded to carbons and in most cases hydrogens bonded to carbons are not acidic hydrogens. Note: For acids, often the donate-able H⁺ are listed first.

K_{a_1} = the acid dissociation constant for the hydrolysis of the original polyprotic acid; K_{a_2} = the acid dissociation constant for the hydrolysis of the conjugate base of the original polyprotic acid; K_{a_3} = the acid dissociation constant for the hydrolysis of the conjugate base of the conjugate base of the original polyprotic acid. Note: Polyprotic acid K_{a_1} , K_{a_2} , K_{a_3} s are often given their own appendix table.

K_{a_1} = The equilibrium constant for the giving of the first H⁺ from polyprotic acid to H₂O

K_{a_2} = The equilibrium constant for the giving of the second H⁺ from polyprotic acid to H₂O.

You'll note that $K_{a1} > K_{a2} > K_{a3}$, since it becomes harder to remove an H^+ from a species that has more of a negative charge.



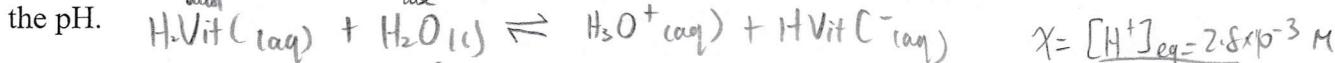
Problem (Weak Polyprotic Acid Template): What is the pH of a 0.10M ascorbic acid

($H_2C_6H_6O_6$) solution? What is the $[C_6H_6O_6^{2-}]$ in this solution? (K_{a1} (ascorbic acid): 7.9×10^{-5} ;

K_{a2} : 1.6×10^{-12}) major species: H_2O , $H_2C_6H_6O_6$, H_2VitC^- 's first dissociation step

dictates pH since $K_{a1}(H_2VitC^-) > K_w$ and $K_{a2}(H_2VitC^-)$

For polyprotic acid problems, ask yourself: What are the major species in the solution and which of these major species dictates the pH? Is the second dissociation step important in determining the pH of the polyprotic acid? Set up your ICE chart and solve the equilibrium expression for the pH.



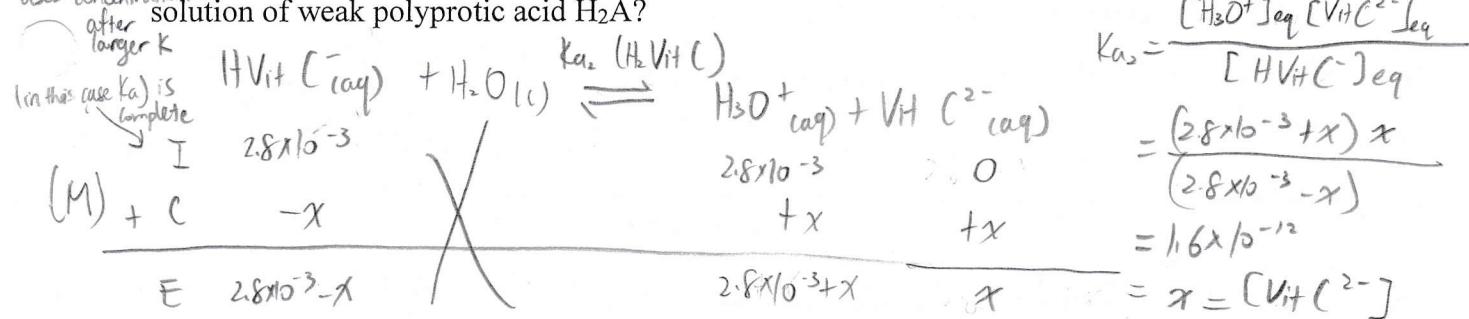
I	0.10	X	0	0
+ C	-x	X	+x	+x
E	$0.10 - x$	(liquid)	x	x

$$\log x = \text{pH} = 2.55$$

(small k approximation)

$$K_{a1} = \frac{[H_3O^+]_{eq}[HVitC^-]_{eq}}{[H_2VitC]_{eq}} = \frac{x^2}{0.10 - x} = 7.9 \times 10^{-5} = \frac{x^2}{0.10}$$

Initial row Part II. What equilibrium creates the species $C_6H_6O_6^{2-}$? Setup the mathematical expression with of ICE chart the appropriate K_a and solve. What do you notice about the concentration of the $[A^{2-}]$ for a weak polyprotic acid H_2A ?



A diprotic base can provide two OH^- (aq) when placed in water. These diprotic bases dissociate in a stepwise fashion with a K_{b1} and a K_{b2} (K_{b1} = equilibrium constant for the dissociation of a given diprotic base in water; K_{b2} = equilibrium constant for the dissociation of the conjugate acid of this diprotic base in water, such that this conjugate acid is acting as a Brønsted-Lowry Base). Keep in mind that the K_{b1} of a diprotic base dictates the pH of the solution and not the K_{b2} (for your purposes). Show the equation for the stepwise hydrolysis of the diprotic base SO_3^{2-} .

Stepwise dissociation for CO_3^{2-}

1st dissociation step K_{b1} of (O_3^{2-})



2nd dissociation step K_{b2} of (O_3^{2-})



Special Diprotic Acid: Sulfuric Acid

What makes sulfuric acid unusual as a polyprotic acid?

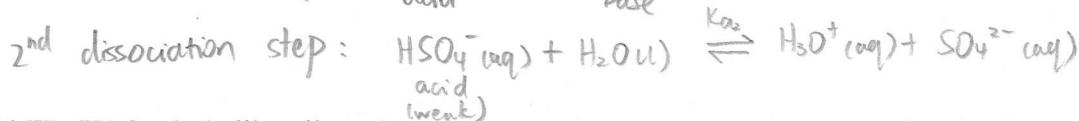
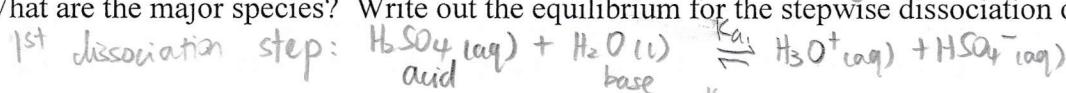
Only polyprotic acid that is a common strong acid

Remember if we know the pH we also know the pOH of a solution

Problem (template for a case where strong acid and weak acid both affect the pH): Calculate the pOH in a solution of 0.0015M H₂SO₄ (K_{a1} : immeasurably large; K_{a2} : 1.2×10^{-2}). Remember that $0.0015 \text{ M H}_2\text{SO}_4 \rightarrow 0.0015 \text{ M H}^+ + 0.0015 \text{ M HSO}_4^- \rightarrow$ Reaction goes to completion.

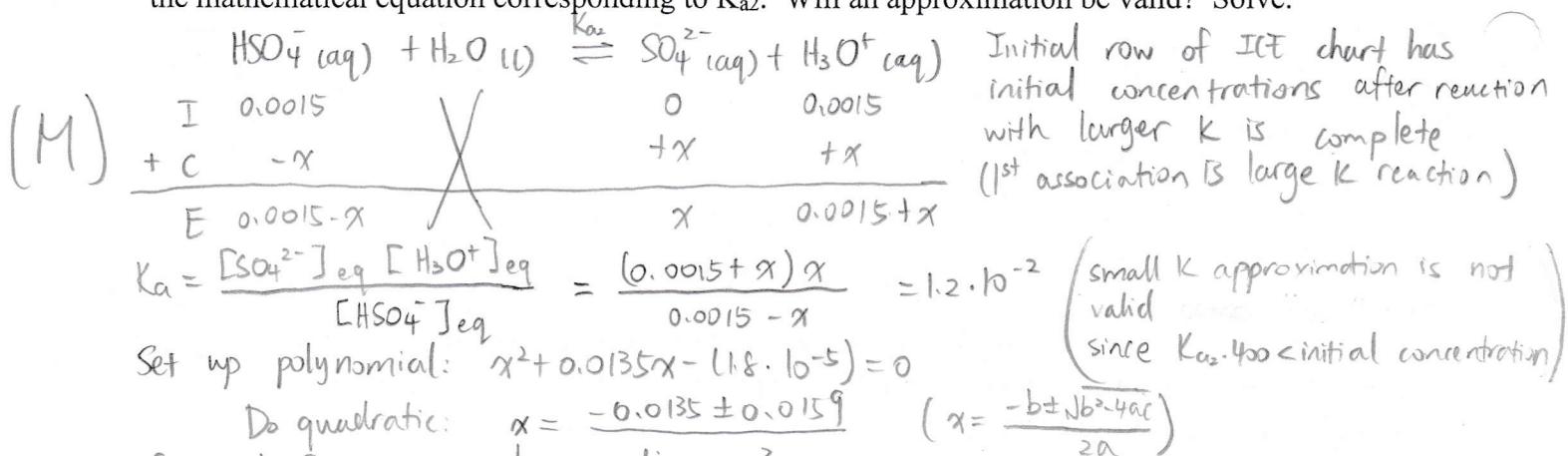
Major species: H₂O, HSO₄⁻, H⁺ (Large K)

What are the major species? Write out the equilibrium for the stepwise dissociation of H₂SO₄.



NOTE: HSO₄⁻(aq), like all **conjugate bases of strong acids**, is not an effective base. Consider that the equilibrium for the reaction H₂SO₄(aq) + H₂O(l) \rightleftharpoons HSO₄⁻(aq) + H₃O⁺(aq) lies overwhelmingly to the right, which means that HSO₄⁻(aq) is unable to deprotonate even H₃O⁺(aq), which is the strongest acid in water. (Think: if a base is unable to deprotonate H₃O⁺, it will also be unable to deprotonate water to make OH⁻(aq).)

Since calculations have demonstrated a **stepwise** dissociation, when considering the second dissociation step equilibrium, we imagine the first dissociation step has already happened. Write the mathematical equation corresponding to K_{a2} . Will an approximation be valid? Solve.



Do quadratic: $x = \frac{-0.0135 \pm 0.0159}{2}$ ($x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$)

Go with \oplus to avoid negative concentrations

$\therefore x = 0.0012$

$[\text{H}_3\text{O}^+]_{\text{eq}} = 0.0015 + x = 0.0027 \text{ M}$ $-\log[\text{H}_3\text{O}^+] = \text{pH} = 2.57$ $14.00 - \text{pH} = 11.43 = \text{pOH}$

Note: Whether one goes + or - with a quadratic should be common-sense (no negative concentrations, "x" won't be greater than the initial concentration, etc...)

Note: as we see, unlike the weak acids where $K_{a1} \gg K_{a2}$, the second dissociation step of especially dilute sulfuric acid has a calculated (and indeed, experimental) impact on the pH of the solution.

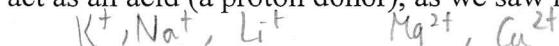
Lecture Concepts 14. Applying Equilibrium Constants to (Aqueous) Solution Chemistry 3.

Calculating the pH of Salt Solutions

Write all the conjugate bases of all 5 common monoprotic strong acids (CBSA = conjugate base of strong acid). Do CBSAs affect the pH of a solution? No.



Remember that HSO_4^- is an exceptional CBSA. Yes, HSO_4^- is a poor base, but remember it does act as an acid (a proton donor), as we saw in the polyprotic acid section.



Alkali metal ions and alkaline earth metal ions are observed to not affect the pH of a solution.

So, without doing a calculation, what will be the pH of a 0.10M KNO_3 solution at 298K?

Thinking about major species, split ionic compound into cation & anion that make up compound

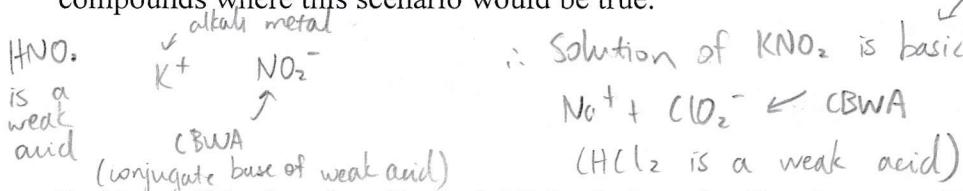
solution is neutral. Major Species: H_2O, K^+, NO_3^- ← CBSA do not affect pH of solution

$\nwarrow \swarrow$ Alkali metal ion

H_2O dictates pH of solution

pH of pure $H_2O = 7.00$

Salts Producing Basic Solutions: A classic scenario of a salt producing a basic solution is when a salt contains alkali metal ion or alkaline earth metal ion as cation and the conjugate base of a (monoprotic) weak acid (conjugate base of a weak acid = CBWA) as anion. List some compounds where this scenario would be true.



For this course, we're considering concentrations of > 0.001M salts.
 $NaClO_4$ is basic.

Problem: Calculate the pH of a 0.15M solution of sodium benzoate ($NaC_7H_5O_2$) (K_a of benzoic acid $HC_7H_5O_2$: 6.4×10^{-5}) @ 25°C.



As always write out the **major species**, remembering as you do so that salts containing an alkali metal are soluble (0.15 M $NaC_7H_5O_2 \rightarrow 0.15$ M Na^+ and 0.15 M $C_7H_5O_2^-$)

Major species: $H_2O, Na^+, C_7H_5O_2^-$ ← Benzoate is a CBWA (it's the conjugate base of benzoic acid whose K_a is small)

\nwarrow alkali metals
don't affect the pH of solution.

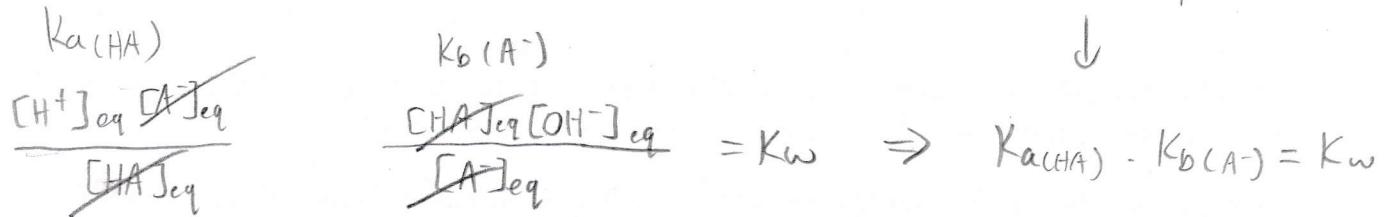
Now, we have the conjugate **BASE** of a (monoprotic) weak acid (CBWA) that dictates the pH here. That's the key word: **BASE**. Think: your solution must be **BASIC** in this case, have a **pH>7**. If you calculate an acidic pH, you've made a mistake!

Now, **THIS** is the **SECRET**. **THIS** is what too many students historically forget with a salt containing a CBWA. You're given the K_a of the weak acid...but **WAIT**, that weak acid isn't even present as a major species!!! (Check those major species. No, no benzoic acid there!)

And besides, the conjugate **BASE** of a weak acid is, well, a **BASE**, so therefore a K_b equilibrium constant regulates the dissociation of the **base** in water! However, the K_b isn't given to us!!! So, how do we determine the K_b of $C_7H_5O_2^-$? We use the K_a of $HC_7H_5O_2$ given to GET the desired equilibrium constant K_b via a calculation!!!

See below derivation using a generic monoprotic weak acid HA and its conjugate base A^- to see how one gets the $K_b(A^-)$ knowing the $K_a(HA)$.

used in a lot of problems

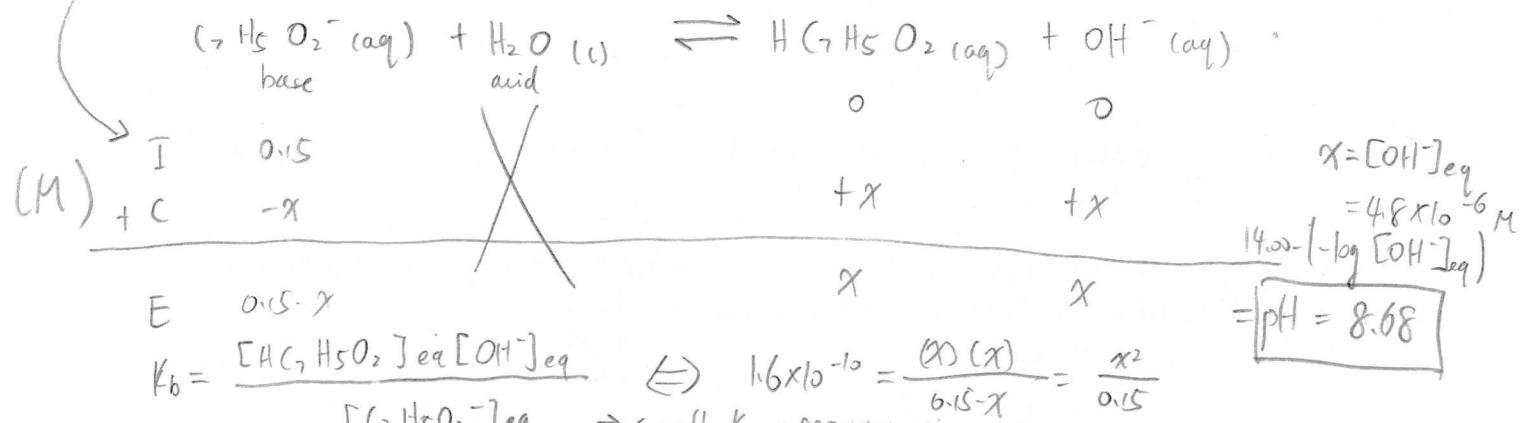


So, let's calculate the K_b of benzoate ($C_7H_5O_2^-$) now. Benzoate is the main source of $[OH^-]$ ions since $K_b \gg K_w$.

$$\frac{K_w}{K_a(HC_7H_5O_2)} = K_b(C_7H_5O_2^-) \quad \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-5}} = 1.6 \times 10^{-10}$$

↑ (NaC₇H₅O₂ in this case)

initial for hydrolysis of CBWA is after ionic compound has split completely
Solve for the pH of 0.15M sodium benzoate into cations & anions.

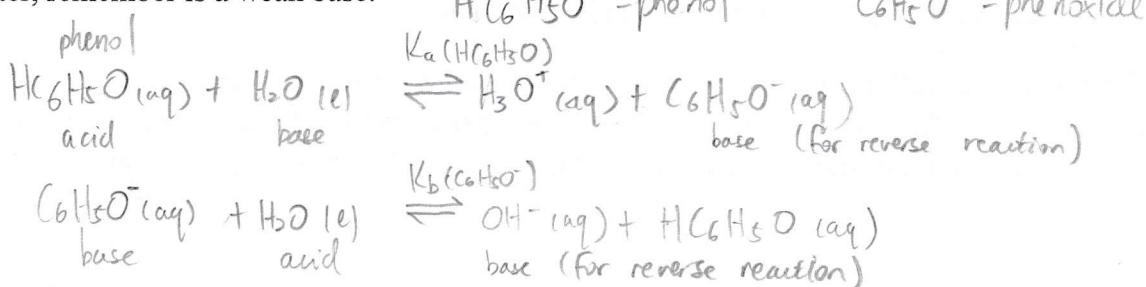


$$K_b = \frac{[HC_7H_5O_2]_{eq} [OH^-]_{eq}}{[C_7H_5O_2^-]_{eq}} \Leftrightarrow 1.6 \times 10^{-10} = \frac{(x)(x)}{0.15 - x} = \frac{x^2}{0.15}$$

\Rightarrow small K approximation

Don't be fooled; the conjugate base of a weak acid we see is also a weak base; the CBWA is just not AS weak a base as the conjugate base of a strong acid. Write the equilibrium equation of HC_6H_5O ($K_a = 1.6 \times 10^{-10}$) and $C_6H_5O^-$ ($K_b = 6.3 \times 10^{-5}$). In terms of basicity $OH^- > C_6H_5O^- > H_2O$.

Water, remember is a weak base.



Salts Producing Acidic Solutions. A classic scenario of a salt producing an acidic solution is when a salt contains the conjugate acid of a weak base as a cation (CAWB= conjugate acid of a weak base) and the conjugate base of a strong acid as an anion (CBSA= conjugate base of a strong acid). List some compounds where this scenario would be true.



A classic scenario of a salt producing acidic solution is the conjugate acid of a nitrogen-containing weak base (weak base has added an H^+) with a negatively-charged CBSA counterion!

Problem: Calculate the pH for a solution of 0.20M pyridinium chloride ($\text{C}_5\text{H}_5\text{NHCl}$) given that the K_b of pyridine ($\text{C}_5\text{H}_5\text{N}$) is 1.7×10^{-9} .

What are the major species? (Remember: ionic compounds with halides or nitrates present are soluble; so 0.20 M $\text{C}_5\text{H}_5\text{NHCl} \rightarrow 0.20 \text{ M } \text{C}_5\text{H}_5\text{NH}^+(\text{aq}) + 0.20 \text{ M } \text{Cl}^-(\text{aq})$)

Major species : H_2O , $\text{C}_5\text{H}_5\text{NH}^+$, Cl^-

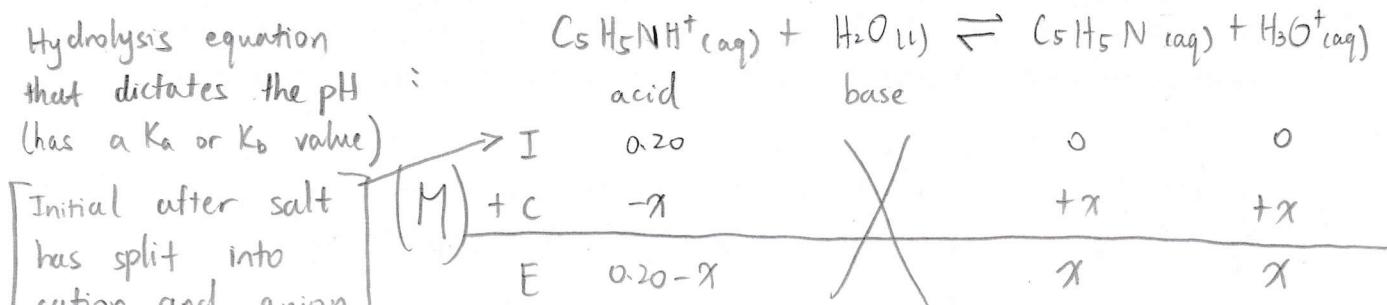
Here, we have a pyridinium ion as the major species that dictates the solution pH. The pyridinium ion is the conjugate **ACID** of a weak base. Should our solution be **ACIDic** or **BASIC**, people?

Acidic

Will it have a K_a or K_b , people? How do we get this constant, people? (Let's get it now.)

$$\text{CAWB has a } K_a (\text{C}_5\text{H}_5\text{NH}^+) = \frac{K_w}{K_b(\text{C}_5\text{H}_5\text{N})} = \frac{1.0 \cdot 10^{-14}}{1.7 \cdot 10^{-9}} = 5.9 \cdot 10^{-6}$$

What major species dictates our pH? Now, solve for the pH...



$$K_a = \frac{[\text{H}_3\text{O}^+]_{\text{eq}} [\text{C}_5\text{H}_5\text{N}]_{\text{eq}}}{[\text{C}_5\text{H}_5\text{NH}^+]_{\text{eq}}} = \frac{x \cdot x}{0.20 - x} = 5.9 \cdot 10^{-6}$$

Small K approximation
 $0.20 - x \approx 0.20$

$$x = 1.1 \cdot 10^{-3} \text{ M} = [\text{H}_3\text{O}^+]_{\text{eq}}$$

$$\text{pH} = -\log x = \boxed{2.96}$$

More Acidic Salt Solutions: Highly-Charged Metal Cations

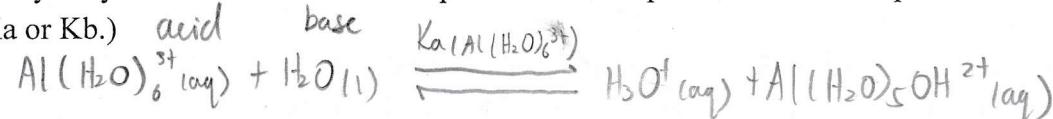
When a highly charged metal ion is present as a cation with a CBSA as anion, an acidic solution is created. (highly charged metal cation = transition metals with 2+ charge or more or aluminum group cations with 3+ charge)

Problem: Calculate the pH of a 0.020M AlBr_3 solution ($K_a: \text{Al}(\text{H}_2\text{O})_6^{3+} = 1.4 \times 10^{-5}$)

major species: $\text{Al}^{3+}, \text{Br}^-, \text{H}_2\text{O}$ CBSA does not affect pH

Based on experimental evidence with electromagnetic radiation, highly-charged metal ions get solvated or in cases where the solvent is water, hydrated so as to form what is known as a complex ion. You should think that for highly charged metal cations in water, that they actually exist as $\text{M}(\text{H}_2\text{O})_n^{x+}$ (aq), where "n" is an integer that varies depending on the metal cation, "x" is the charge of the metal cation and M is the metal. So, Al^{3+} (aq) = $\text{Al}(\text{H}_2\text{O})_6^{3+}$ (aq). (solvated= surrounded by solvent but involving attractive forces; hydrated= solvated by water; $\text{M}(\text{H}_2\text{O})_n^{x+}$ (aq) = hydrated metal species)

Dissociate first: $0.020 \text{ M AlBr}_3 \rightarrow 0.020 \text{ M Al}^{3+} + 0.060 \text{ M Br}^-$
Write the chemical equation for the hydrolysis of $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and solve for the pH. (Keep in mind that a hydrolysis refers to a chemical equation whose equilibrium has an equilibrium constant K_a or K_b .)



(M)	I	0.020			0	0
	+ C	-x			+x	+x
	E	0.020-x			x	x
$K_a = \frac{[\text{H}_3\text{O}^+]_{\text{eq}} [\text{Al}(\text{H}_2\text{O})_5\text{OH}^{2+}]_{\text{eq}}}{[\text{Al}(\text{H}_2\text{O})_6^{3+}]_{\text{eq}}}$					$x = [\text{H}_3\text{O}^+]_{\text{eq}} = 5.3 \times 10^{-4}$	

$$1.4 \times 10^{-5} = \frac{(x)(x)}{0.020-x} = \frac{x^2}{0.020} \leftarrow \text{small } K_a \text{ approximation}$$

$$-\log x = \boxed{\text{pH} = 3.28}$$

Vocabulary: **ligand**= lone-pair or π electron bearing-species whose lone pairs or pi electron pair form a covalent bond to a metal ion; **complex ion**= a metal ion surrounded by ligands.

coordination number = number of ligands that surround the metal ion; **pi electron**= electron in a pi bond.

What is the ligand, the complex ion and coordination number for $\text{Al}(\text{H}_2\text{O})_6^{3+}$?

Ligand: H_2O Complex Ion: $\text{Al}(\text{H}_2\text{O})_6^{3+}$ Coordination Number: 6

The coordination number is not necessarily 6 for the hydration of highly-charged metals, for example Zn^{2+} (aq)= $\text{Zn}(\text{H}_2\text{O})_4^{2+}$ (aq). You are not expected to know by heart the coordination number by which ligands surround a given metal cation. You should assume that whatever hydrated metal species given to you in a problem is the correct hydrated major species whose K_a should be used for pH determination.

For salts with CBWA/CAWB combinations, one predicts acidity, basicity and neutrality only

Salts composed of CBWA (Conjugate base of a weak acid) and CAWB (Conjugate acid of a weak base) combinations

So, salts made up of CBWA and CAWB combinations have a cation AND an anion such that both ions affect the acidity or basicity of a solution. In our great kindness, we will not ask you to calculate the pH of these solutions (you will learn how to calculate the pH of such salts in an advanced analytical chemistry course). One might be asked, however, to determine if the salt solution is acidic, basic or neutral.

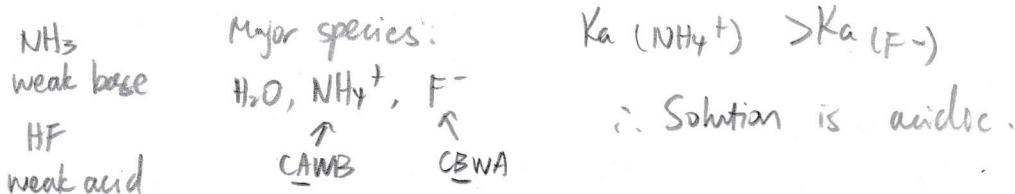
So, all you need to do remember is these general predictive rules (think that these rules hold true even if the anion: cation ratio is not 1:1).

If the K_a (cation) $> K_b$ (anion) the solution is circle → acidic basic neutral.

If the K_a (cation) = K_b (anion) the solution is circle → acidic basic neutral.

If the K_a (cation) $<$ K_b (anion) the solution is circle → acidic basic neutral.

Example: A 0.10M NH₄F solution, is it acidic, basic or neutral? $K_a(\text{NH}_4^+)$: 5.6×10^{-10} , $K_b(\text{F}^-)$: 1.4×10^{-11} . Write out your major species!



Ions That Can Act as Either Acids or Bases

While most ions/aqueous solutes that have acidic or basic properties you should assume can either only act as Bronsted-Lowry bases or only act as Bronsted-Lowry acids in water, there are amphoteric ions. The ions that can act as both proton donors and proton acceptors (such as HCO₃⁻ and HSO₃⁻) can be recognized since such ions can be both acids and bases in water, since one will obtain both a K_a and a K_b value for these ions.

A solution of 0.10M sodium bicarbonate (NaHCO₃) given that the $K_b(\text{HCO}_3^-)$ = 2.3×10^{-8} and that the K_{a2} for H₂CO₃ = K_a for HCO₃⁻ = 5.6×10^{-11} . Is this solution acidic, neutral or basic?

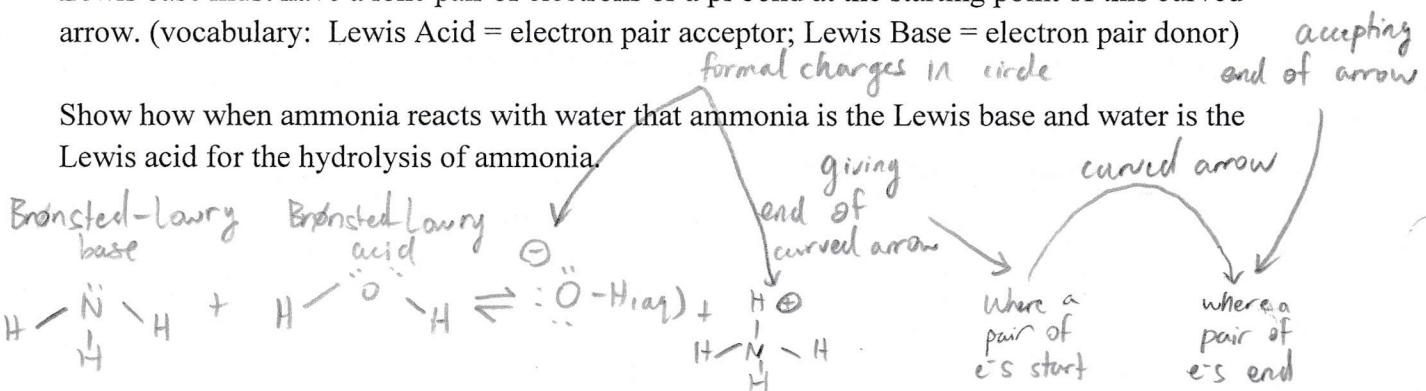
Major species: H_2O , Na^+ , HCO_3^-
 ↗ alkali metals don't affect
 the pH of the solution

One needs to compare the K_a and the K_b of an amphoteric ion to figure out whether it makes the solution acidic, basic or neutral.
 Since $K_b(\text{HCO}_3^-) > K_a(\text{H}_2\text{CO}_3)$

Lecture Concepts 15. Predicting Relative Acidity and Basicity Looking at Molecular Structure with Lewis Acid/Lewis Base Definition.

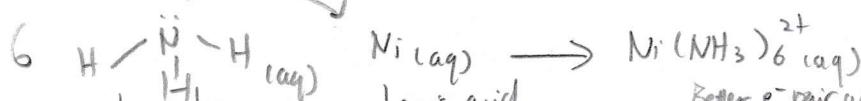
As we start looking at molecular structure (molecular structure = Lewis structure) to predict the relative acidity or basicity of various molecules/ions, it is useful to expand the way we think about acids and bases to a more inclusive definition of acids and bases than the traditional Brønsted-Lowry definition we've been considering so far. That is, the Lewis acid/Lewis base definition.

In acid-base reactions we've considered so far, a Brønsted-Lowry acid is coupled with (reacts with) a Brønsted-Lowry base. That is, we have an H^+ acceptor (the Brønsted-Lowry Base) which accepts the H^+ from the H^+ donor (the Brønsted-Lowry Acid). However, acids and bases may be defined by the Lewis acid/Lewis base definition, such that the Lewis acid is at the accepting end of the curved arrow between reactants and the Lewis base is at the giving end of the curved arrow between reactants. A Lewis base is always coupled with the Lewis acid. The Lewis base must have a lone pair of electrons or a pi bond at the starting point of this curved arrow. (vocabulary: Lewis Acid = electron pair acceptor; Lewis Base = electron pair donor)



All Brønsted-Lowry acids in a reaction are Lewis acids and all Brønsted-Lowry bases are Lewis bases. There are however Lewis acids that are not Brønsted-Lowry acids and Lewis bases that are not Brønsted-Lowry bases in reactions where there is no proton transfer (proton= H^+).

Problem: Consider the interaction of ligands with metal to make a complex ion (e.g., $\text{Ni}^{2+} + 6\text{NH}_3 \rightarrow \text{Ni}(\text{NH}_3)_6^{2+}$). Draw structures. Label the Lewis acid and base. Just looking at the reacting species, how would you know what is the Lewis acid and base?

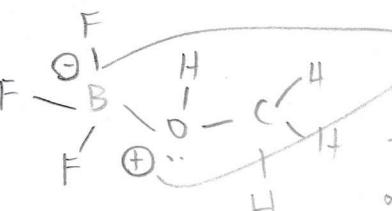
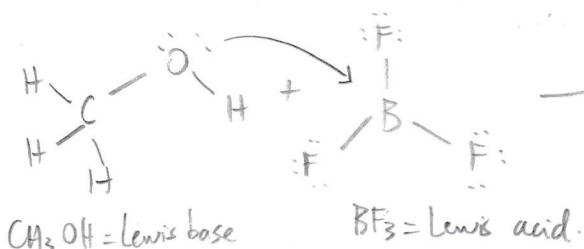


→ Think Ni^{2+} is positively-charged and cations are more likely to be electron-pair acceptors (or Lewis acid)

Logic: What do you think is a stronger Lewis acid, Fe^{2+} or Fe^{3+} ? strong Lewis acid

Fe^{3+} having a greater value of positive is the better e⁻ pair acceptor.

Problem: Consider the reaction $\text{BF}_3 + \text{CH}_3\text{OH} \rightarrow \text{F}_3\text{BOHCH}_3$. Draw structures below and label the Lewis acid and Lewis base, and rationalize your choice of Lewis acid and Lewis base.



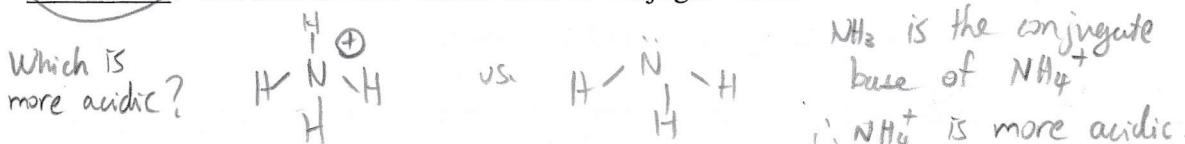
In circles are formal charges.

Think: boron has an incomplete octet so has space to accept an e⁻ pair, which makes BF_3 a good Lewis acid.

Section: Using Molecular Structure to Predict Acidity and Basicity of substances

For this section we consider exclusively acids and bases that fall under the Brønsted-Lowry Acid/Base category.

Initial Rule: An acid is more acidic than its conjugate base.



When wishing to determine relative acidity of two acids, say to yourself this mantra:

Mantra: THE STRONGER THE ORIGINAL ACID (HA), THE MORE STABLE ITS CONJUGATE BASE (A^-). (Remember: the stronger acid = the more reactive acid = the acid with the most readily lose-able H^+ = the more acidic acid; keep in mind that a conjugate base is a type of base)

For all future rules in the section, we will look at the stability of the conjugate bases of 2 acids to determine the relative strength of these 2 acids. One should only use molecular structure to compare stability of bases when the formal charge on the *atom bearing the negative charge* is the same for both bases. (Vocabulary: the atom bearing the negative charge = the atom that was attached to the most acidic hydrogen in the conjugate acid of a base)

H_3O^+ is the conjugate acid of H_2O NH_4^+ is the conjugate acid of NH_3

Remember: The more stable the base, the less reactive and the weaker base it is. The stronger the original acid, the weaker the bond to the donated H will be.

4 RULES TO DETERMINE THE RELATIVE STABILITY OF TWO BASES

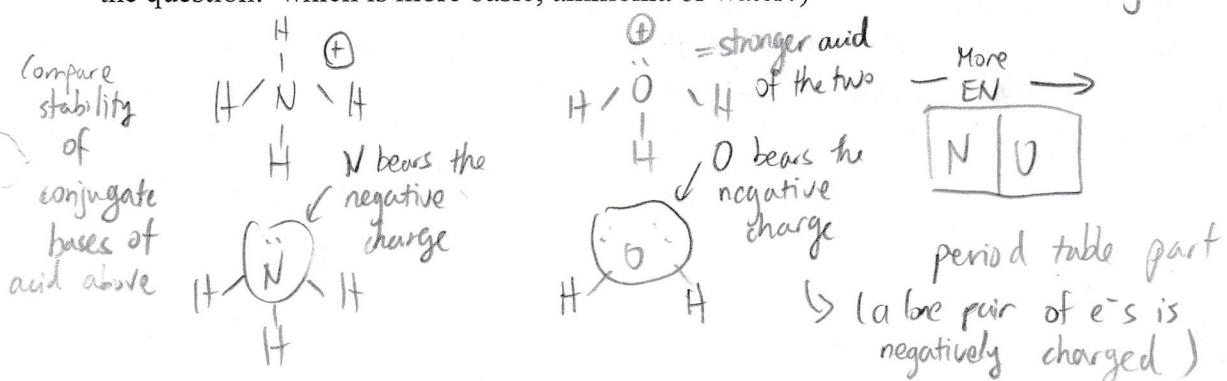
RULES 1 and 2: These rules apply ONLY when the atom bearing the negative charge in the base is different for two bases being compared.

Rule 1. Comparing the electronegativity of the atom bearing the negative charge in bases

When one compares two atoms in the **same period** (row) of the periodic table bearing the negative charge in two bases, one looks at the electronegativity of these two atoms to determine the stability of the bases. The more electronegative an atom (across a period) bearing the negative charge, the more protons the atom has to hold the extra electrons, therefore the more stable the base that has this more electronegative atom.

Problem: What is a stronger acid, ammonium or hydronium? (Note how we also address here the question: which is more basic, ammonia or water?)

$\text{EN} = \text{electronegative}$

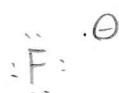


Formal charges in circles

Problem: What's a stronger base, hydroxide or fluoride?



hydroxide is stronger base



more stable
base = weaker base

mini-period table

O	F
---	---

- more \rightarrow
EN

Rule 2. Comparing the size of atoms bearing the negative charge in bases.

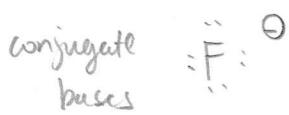
When examining **atoms in the same group or column** of the periodic table that bear the negative charge, the **size of atoms bearing the negative charge** in two bases being compared dictates the relative stability of bases. Exclusively for two atoms in the same group/column, the larger atom of two atoms bearing the negative charge has the negative charge spread out over a larger volume, which causes the base with this larger atom to be more stable.

Note the difference with Rule 1! One does not look at the electronegativity of the atoms bearing the negative charge in bases to determine stabilities of bases when comparing atoms in the same group/column of the periodic table!

Question: Which is more acidic? HF or HI

HI is acidic, more acidic

Draw their conjugate bases:



more stable base

mini-period table

F		↓
I		

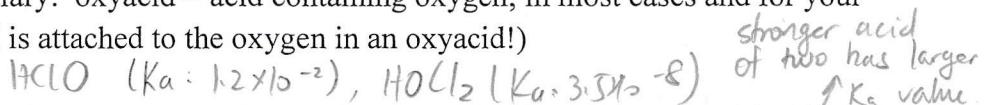
Increase
in size

Think: The more concentrated the negative charge, the less stable the base (higher in potential energy), the more reactive the base, the more basic the base.

Question: Why does electronegativity dictate stability of bases that contain atoms bearing the negative charge in the same period within bases while size dictates the stability of bases that contain atoms bearing the negative charge in the same group of the periodic table? Answer: Ultimately, the theory changes in order to match experimental data: remember that the K_a/K_b and therefore the acidity/basicity can be determined experimentally. One suggestion I have is that as one goes down a group, atomic size increases become important as one adds electrons to a new shell, while the atomic size is a less important factor moving across a period

Rules 3 and 4. Use rules 3 and 4 when the atom bearing the negative charge is the SAME for the two conjugate bases being compared.

Rule 3. Resonance/delocalization. Typically (in MOST cases), the more resonance structures one can draw for a given base, the more the negative charge is spread out by delocalization and consequently the more stable the base. This explains the following observed phenomenon: **The more oxygens attached to a given non-hydrogen atom in a given oxyacid, the stronger the acid will be.** (Vocabulary: oxyacid = acid containing oxygen; in most cases and for your purposes always, the H is attached to the oxygen in an oxyacid!)



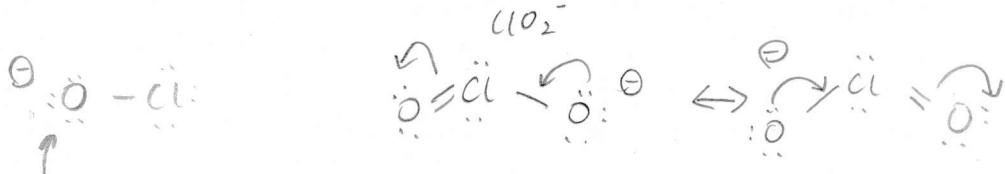
Problem: Attach the correct K_a to each of the following acids: hypochlorous acid, chlorous acid (K_a choices: 3.5×10^{-8} , 1.2×10^{-2})



Draw the molecular formula and conjugate base for each acid, including all resonance structures.

Draw

Conjugate
Base



The conjugate bases of most oxyacids, an oxygen bears the negative charge.

Remember: When drawing all valid resonance structures, one draws all valid Lewis structures where sigma bonds and the symbols representing nuclei and core electrons are placed in the same position, but the *electrons are located on or between different atoms on paper*.

Remember: When one can draw more than one valid Lewis structure, we think about the actual structure from experiment as being a hybrid of all the valid Lewis structures. The pi bond electrons or lone pair electrons are said to be delocalized (delocalized= spread out) by resonance according to the curved arrows that show how resonance structures interrelate.

Rule 4. Inductive Effect to Determine Relative Stability of Two Bases

For this rule, one looks at atoms NEARBY the atom bearing the negative charge in two bases.

If an electronegative atom (such as F, O, N, Cl, Br or I) is located close to an atom bearing a negative charge, the electron-attracting atom can pull electrons toward itself, thereby pulling somewhat the negative charge away from the atom bearing the charge in the Lewis structure, thereby stabilizing the negative charge of the base somewhat by delocalization. (vocabulary: the pulling of electrons by an electron-attracting atom (or group of atoms)= inductive effect)

The more electronegative the atom, the greater the inductive effect (F more electronegative than Cl which is more electronegative than Br which is more electronegative than I, for example)

Problem: Attach the following K_a values to the following acids HOBr vs. HOI according to expectation (K_{as} : 2×10^{-11} , 2×10^{-9}). HOI has a K_a of 2×10^{-11}

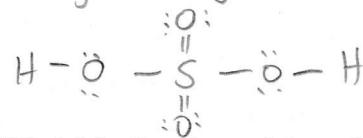
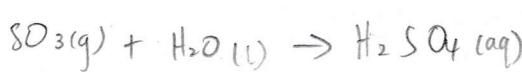
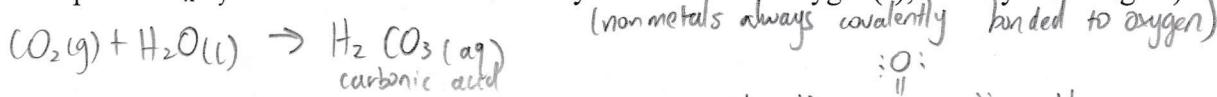
HOBr has a K_a of 2×10^{-9} being stronger acid.

Draw the conjugate bases. Which is more stable?



more stable base of two since Br spreads out the negative charge on oxygen better by inductive effect.
Acid/Base Properties of Oxides (oxide = anhydride)

When a covalent oxide is dissolved in water, an acidic solution will result. Similarly, a molecule where an atom is attached to an $-\text{OH}$ group such that this atom is covalently bonded to the oxygen, an acidic solution will result. Note how when a covalent oxide (let's show with carbon dioxide) is dissolved in water the two hydrogens and the oxygen of the water end up in the same molecule as the covalent oxide, so as to make a known acid. (covalent oxide = compound $A_x\text{O}_y$ where atom A is covalently bonded to the oxygen(s); x and y are integers)



Note: The presence of $\text{H}_2\text{CO}_3(\text{aq})$ in water due to the $\text{CO}_2(\text{g})$ in the air explains why the pH of distilled water is observed to be acidic in labs rather than with a pH=7.0.

However, when one has an ionic oxide, the ionic bond will dissociate in solution and a basic solution will result since $\text{O}^{2-}(\text{aq})$, a super-powerful base, reacts completely with water to give 2 $\text{OH}^-(\text{aq})$. (basic oxide = basic anhydride = ionic oxide = compound $M_x\text{O}_y$ where the metal M is ionically bonded to the oxygen). Alkaline earth and alkali metals are ionically bonded to the oxygen in oxides.

Calculate the pH of a 0.1M Na_2O solution.

Major species after dissociation: H_2O , Na^+ , O^{2-}

$\text{O}^{2-}(\text{aq})$

super-power

base

(stronger than $\text{OH}^-(\text{aq})$)

Reaction

$\longrightarrow 2\text{OH}^-(\text{aq})$

acid

Due to the 1:2 mole ratio of $\text{O}^{2-} : \text{OH}^-$, for every 0.1M O^{2-} one has initially, there will be 0.2M OH^- in solution produced.

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

$$\text{pOH} = -\log(0.2) = 0.7$$

$$14.00 - \text{pOH} = \text{pH} = 13.3$$

Any base

Stronger than

OH^- deprotonates

H_2O

Chapter 15 Zumdahl

Lecture Concepts 16. Applying Equilibrium Constants to (Aqueous) Solution Chemistry 5.

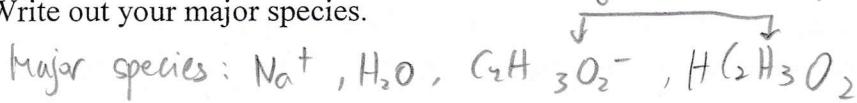
Common Ion Effect and Calculating the pH of Buffered Solutions

Common ion effect = shift in equilibrium position caused by the addition of an ion already involved in an equilibrium reaction.

Common Ion Effect

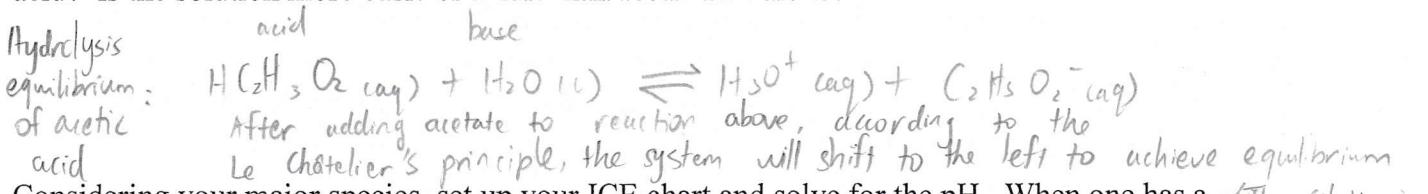
Problem: Calculate the pH of a solution containing 0.20M acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) and 0.30 M sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$). (Think: $0.30 \text{ M NaC}_2\text{H}_3\text{O}_2 \rightarrow 0.30 \text{ M Na}^+ + 0.30 \text{ M C}_2\text{H}_3\text{O}_2^-$)

Write out your major species.



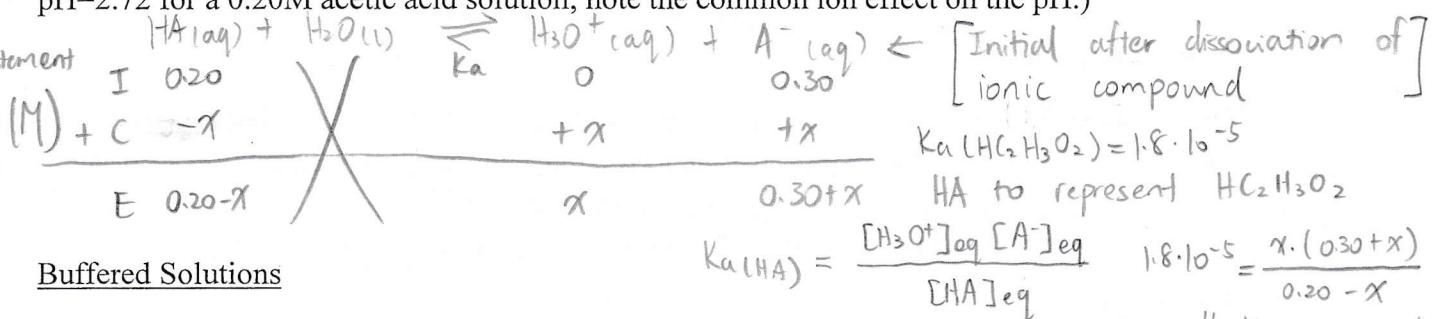
conjugate acid-base pair

What effect does the addition of sodium acetate have on the hydrolysis equilibrium of acetic acid? Is the solution more basic or acidic than acetic acid alone?



Considering your major species, set up your ICE chart and solve for the pH. When one has a conjugate acid-base pair both present as major species you may use either the hydrolysis associated with the K_a of the acid or the hydrolysis associated with K_b of the base in the conjugate acid-base pair to determine equilibrium concentrations. I'm going to use the K_a for acetic acid, but you could just as easily use the K_b for acetate and get the same answer (The pH=2.72 for a 0.20M acetic acid solution; note the common ion effect on the pH.)

The solution will be more basic as the $[\text{H}_3\text{O}^+]$ decreases



Buffered Solutions

Q: What is a buffer (buffer = buffered solution)?

A buffer is a solution resistant to pH change.

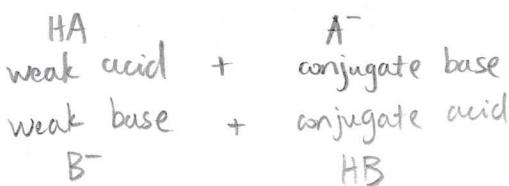
Q: Why should one care about buffers?

A buffer can be helpful since

1) certain reactions occur in a narrow pH range;

2) biological systems can exist within a certain pH range.

A buffer solution is composed of a weak acid solute and its conjugate base or a weak base solute and its conjugate acid.



$$x = [\text{H}^+] = 1.2 \cdot 10^{-5}$$

$$-\log [\text{H}^+] = \boxed{\text{pH} = 4.92}$$

The more concentrated each of the components are, the better the buffer will be. Why do you think it's important to have both components (weak acid solute AND its conjugate base or weak base solute AND its conjugate acid) present in a buffer?

The weak acid solute will prevent significant pH changes upon adding base, while the conjugate base solution prevents significant pH changes upon adding acid.

Problem: Calculate the pH of a 1.0L mixture of 0.30M HF and 0.30MNaF after the addition of 0.01 mol NaOH. Note that the pH= 3.14 before the addition of NaOH. Assume no volume change on adding the NaOH. ($K_a(HF) = 7.2 \times 10^{-4}$) (Remember: $0.30 \text{ M NaF} \rightarrow 0.30 \text{ M Na}^+$ and 0.30 M F^-) To calculate pH problems, always dissociate ionic compounds first! (into anion and cation) $0.01 \text{ mol NaOH} \rightarrow 0.01 \text{ mol Na}^+ + 0.01 \text{ mol OH}^-$

The strong base $\text{OH}^-(\text{aq})$ reacts with strong or weak acids completely in Brønsted-Lowry acid-base reactions and the strong acid $\text{H}^+(\text{aq})$ reacts with either strong or weak bases completely in Brønsted-Lowry acid-base reactions.

solutes

So, the FIRST thing you do for problems where you have a reaction going to completion (such as between strong base or strong acid and one of the components in the buffer) is to deal with the reaction that goes to completion first before looking at smaller K values. (Reaction going to completion = large K reaction) For the large K reaction part, first, we consider the amounts of each reagent and product present in a hypothetical "before the large K reaction has occurred".

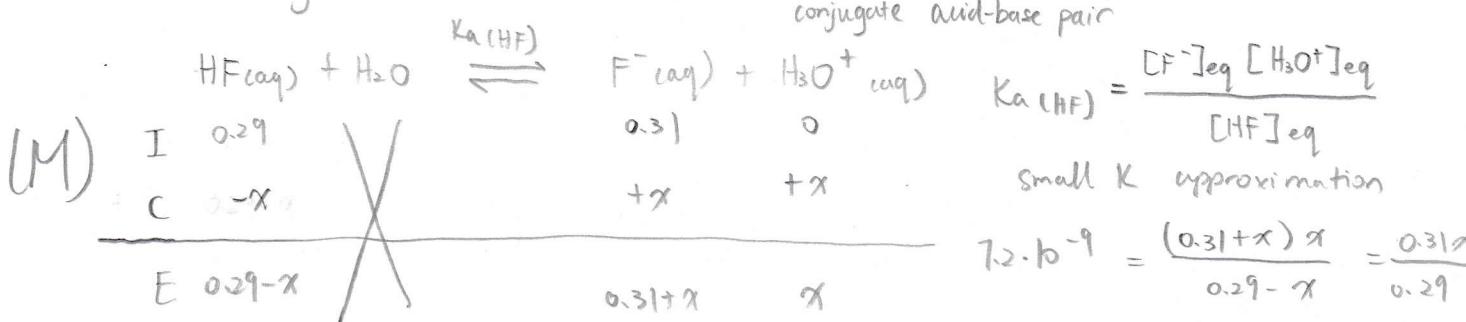
Then we write the amounts after this large K reaction has taken place.

				$\xrightarrow{\text{LR} \rightarrow \text{all LR. in large K reaction}}$
Large K reaction:	HF	+	OH^-	$\rightarrow \text{F}^-$
Before Large K reaction:	0.30		0.01	0.30
Change:	-0.01		-0.01	+0.01
After Large K reaction:	0.29		0	0.31

↓
after ionic compound dissociates

Then, once our large K reaction has taken place, we consider the smaller K hydrolysis second. Since we have a conjugate acid-base pair, we can look at the equilibrium for the hydrolysis of the $\text{HF}(\text{aq})$. Write out the major species, the equilibrium expression and solve. Note how the $[\text{HF}]$ and $[\text{F}^-]$ concentration in the "I" row of the ICE chart are the same as the $[\text{HF}]_{\text{eq}}$ and $[\text{F}^-]_{\text{eq}}$.

Consider major species after large K reaction is complete: F^- , HF , H_2O , Na^+ (does not affect pH)
conjugate acid-base pair



$$-\log x = \boxed{\text{pH} = 3.17}$$

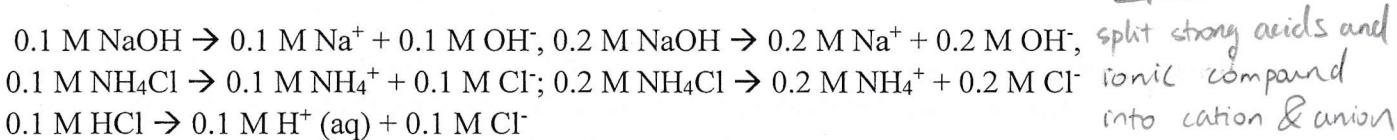
↳ makes sense, pH changed slightly as expected for buffer.

Remember that in a buffer problem, the pH should not change much after adding a strong acid or strong base to a buffered solution, which is a way of double-checking your answer when acid or base is added to a buffer.

Problem: Circle all of the following solutions that make a buffered solution.

- a) 0.1 M NaOH, 0.1 M NH₃
- b) 0.1 M NaOH, 0.2 M NH₄Cl
- c) 0.1 M HCl, 0.2 M NH₃
- d) 0.1 M NH₃, 0.2 M NH₄Cl

Note: You need to be careful when thinking about whether you have a buffer. Think: do you have a buffer after all the large K reactions have occurred? If you do, you have a buffer. Step 1:



- a) Solution a) has two bases, OH⁻, NH₃. Two bases can't react together, there's no conjugate acid-base pair solutes, so consequently there's no buffer here. Although NH₃ does dissociate to produce a small amount of NH₄⁺, having a weak base solute and a small amount of its conjugate acid is not sufficient to make a buffer, as will be described on the next page.
- b) Remember, OH⁻(aq) is a strong base that can react completely in a large K reaction with NH₄⁺(aq) since NH₄⁺ is an acid (NH₄⁺ is the conjugate acid of a weak base, so is consequently an acid).

			L.R.	OH ⁻ + NH ₄ ⁺ → NH ₃	→ goes to completion
Before Large K reaction:	0.1	0.2	0	(M)	After large K reaction is complete, since I have a weak base solute (NH ₃) and its conjugate acid (NH ₄ ⁺) both present
Change	-0.1	-0.1	+0.1		→ I have a buffer
After Large K reaction	0	0.1	0.1		

- c) Remember H⁺(aq) is a strong acid that can react completely with any base and NH₃, as we know, is a weak base.

			L.R.	H ⁺ + NH ₃ → NH ₄ ⁺	base
Before Large K reaction:	0.1	0.2	0	(M)	
Change	-0.1	-0.1	+0.1		
After Large K reaction	0	0.1	0.1		← same explanation

- d) 0.1 M NH₃ and 0.2 M NH₄⁺ are present in the solution, so therefore a weak base solute and its conjugate acid are present, so a buffer IS present.

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

Preparing a Buffer of a Given pH

So, as long as the concentration of HA (generic weak acid) ~~or~~ A⁻ (its conjugate base) is large relative to the amount of OH⁻ or H⁺ added, little change will result in the pH of the solution.

To prepare a buffer of a given pH, we can simply re-arrange the expression for Ka and we'll see that by choosing a given [HA]/[A⁻] ratio, we will get a solution of a certain [H⁺] concentration. For a buffer, as you saw in the problem with HF and F⁻, the [HA]_{eq} is essentially equal to the [HA]_i and the [A⁻]_{eq} was essentially equal to the [A⁻]_i, such that [HA]_i and [A⁻]_i are the concentrations of [HA] and [A⁻] after the large K reactions are complete.

$$[H^+] = K_a \left(\frac{[HA]_i}{[A^-]_i} \right) \rightarrow \text{This equation one can use for find } [H^+] \text{ in a buffer only.}$$

Or alternatively, if we take the -log of both sides of the above equation and rearrange, we will get the **Henderson-Hasselbalch equation**, an equation useful for problem solving that is only used for buffers. Sometimes students forget whether the [A⁻] or [HA] is on top in the shown ratio; what's an easy way to remember this?

$$-\log [H^+] = -\log (K_a \frac{[HA]_i}{[A^-]_i}) \quad pH = -\log K_a - \log \left(\frac{[HA]_i}{[A^-]_i} \right) \quad (-\log x = \log x^{-1})$$

Henderson-Hasselbalch equation: $pH = pK_a(HA) + \log \left(\frac{[A^-]_i}{[HA]_i} \right)$ → Equation used for finding pH of buffered solution only.

There's also the **Henderson-Hasselbalch equation for pOH**, also only used for buffers, which we can get by taking the -log of both sides of the equation [OH⁻]=K_b[B]_i/[BH⁺]_i and rearranging ([B]_i is the concentration of weak base solute and [BH⁺]_i is the concentration of the weak base's conjugate acid after the large K reactions are complete). Show this below.

$$\begin{aligned} -\log [OH^-] &= -\log (K_b \cdot \frac{[B]_i}{[BH^+]_i}) \\ \Leftrightarrow pOH &= -\log K_b - \log \left(\frac{[B]_i}{[BH^+]_i} \right) \end{aligned} \rightarrow \text{Rearrange to get Henderson-Hasselbalch equation for pOH:}$$

$$pOH = pK_b + \log \left(\frac{[BH^+]_i}{[B]_i} \right)$$

Buffering capacity = the ability of a buffered solution to absorb protons or hydroxide ions H⁺ without a significant change in pH.

For optimal buffering capacity, the following two points must be true:

- concentrations of [A⁻] and [HA] must be high. High = $\geq 0.01M$
- The [A⁻]/[HA] ratio should be close to 1 (optimal buffering capacity is said to be within this [A⁻]/[HA] ratio range: 0.1 to 10).

Why is point #2 true for buffers?

One wants the buffer to be similarly resistant to pH change when acid is added as it is when base is added.

$$\text{pH} = \text{pK}_a(\text{HA}) + \log \left(\frac{[\text{A}^+]_i}{[\text{HA}]_i} \right)$$

$$\log (1.1) = -1$$

$$\log (1.0) = 0$$

Since one wants an $[\text{A}^-]/[\text{HA}]$ ratio in this range: $0.1 \leq [\text{A}^-]/[\text{HA}] \leq 10$, if one wants to prepare a buffer with a pH = x, from the Henderson-Hasselbalch equation, the weak acid HA one should choose as a part of the HA and A^- mixture to create optimal buffering capacity would be a weak acid HA that has a $\text{pK}_a = x \pm 1$. Having a $\text{pK}_a = x$ of this weak acid HA component is said to create the most optimal buffer.

Problem: What is the pH if 400. mL of 0.55M lactic acid ($\text{HC}_3\text{H}_5\text{O}_3$) is mixed with 600. mL of 0.55 M sodium lactate ($\text{NaC}_3\text{H}_5\text{O}_3$)? ($K_a(\text{lactic acid}) = 1.4 \times 10^{-4}$)

(Remember: $0.55 \text{ M NaC}_3\text{H}_5\text{O}_3 \rightarrow 0.55 \text{ M Na}^+ + 0.55 \text{ M C}_3\text{H}_5\text{O}_3^-$) \rightarrow lactate

To find pH of solution, we need to consider the concentration of lactate & lactic acid once mixed together:

$$C_1V_1 = C_2V_2$$

$$(0.55 \text{ M lactic acid})(400. \text{ mL}) = C_2(1000. \text{ mL})$$

$$C_2 = 0.22 \text{ M } \text{HC}_3\text{H}_5\text{O}_3$$

similar ration

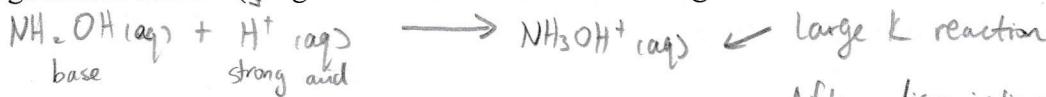
$$\text{pH} = \text{pK}_a(\text{HC}_3\text{H}_5\text{O}_3) + \log \left(\frac{[\text{C}_3\text{H}_5\text{O}_3^-]_i}{[\text{HC}_3\text{H}_5\text{O}_3]_i} \right)$$

$$= -\log (1.4 \cdot 10^{-4}) + \log \left(\frac{0.33}{0.22} \right) \Leftrightarrow \boxed{\text{pH} = 4.03}$$

One More Buffer Problem: Calculate the pH of a solution where 0.02 mol HNO_3 is added to a 1.00 L mixture of 0.200 M hydroxylamine (NH_2OH) and 0.200 M NH_3OHCl . Before adding the 0.02 mol HNO_3 , the pH of the solution is 6.04. Assume no change in volume upon adding the HNO_3 . $K_b(\text{NH}_2\text{OH}) = 1.1 \times 10^{-8}$ (Remember: $0.02 \text{ mol HNO}_3 \rightarrow 0.02 \text{ mol H}^+ + 0.02 \text{ mol NO}_3^-$; $0.200 \text{ M NH}_3\text{OHCl} \rightarrow 0.200 \text{ M NH}_3\text{OH}^+ + \text{Cl}^-$)

limiting reagent \nearrow First, dissociate strong acid/ionic compound into cations/anions

Then Large K reaction 1st. (Large K reaction considered: strong acid reacts with weak base present)



(M)	Before large K reaction	0.200	0.02	0.200	above	conjugate acid-base pair
	change	-0.02	-0.02	+0.02	Major species after large K reaction	$\text{NH}_2\text{OH}, \text{NH}_3\text{OH}^+$
	After large K reaction	0.18	0	0.22	$\text{H}_2\text{O}, \text{NO}_3^-, \text{Cl}^-$	CBSA don't affect pH

Small K hydrolysis reaction second to determine pH. (Since we have a buffer, we may use a Henderson-Hasselbalch equation to determine pH using the small K, K_b .)

$$\text{pOH} = \text{pK}_b(\text{NH}_2\text{OH}) + \log \left(\frac{[\text{NH}_3\text{OH}^+]_i}{[\text{NH}_2\text{OH}]_i} \right)$$

i = initial
refers to the initial concentration after large K reaction is complete

$$\text{pOH} = -\log (1.1 \times 10^{-8}) + \log \left(\frac{0.22 \text{ M}}{0.18 \text{ M}} \right)$$

$$14.00 - \text{pOH} = \boxed{\text{pH} = 5.95} \quad \leftarrow \text{Makes sense, pH changes very little after adding HNO}_3.$$

Lecture Concepts 17. Applying Equilibrium Constants to (Aqueous) Solution Chemistry 6.

Titrations and Indicators.

During a titration, plotting the pH versus the volume of titrant added is called a titration curve or a pH curve. (see curves in notes)

There are four varieties of curves we'll consider here. If given a titration problem, it will fall under one of the following four varieties (note **analyte** is listed first- **titrant** second). We are not looking at titrations of polyprotic acids or dibasic bases for this course.

1. Strong acid- strong base titration
2. Strong base-strong acid titration
3. Weak acid-strong base titration
4. Weak base-strong acid titration

For considering titrations, essentially what you need to do is:

- 1) Remember, as before, that a strong acid will react COMPLETELY with any base (weak or strong) present and that a strong base will react COMPLETELY with any acid (weak or strong) present ← Large K reactions will occur first. *(after dissociating ionic compound / strong acids into cations / anions)*
- 2) Once the large K reaction is complete, think what major species are present and which of those species will dictate the pH? If that species produces H⁺ (or OH⁻) via a hydrolysis equilibrium, then set up your ICE chart and equilibrium expression accordingly.

Template 1. Strong acid-strong base titration

We have a solution of 30.0 mL of 0.100 M HCl (HCl is the analyte) and are titrating the solution with 0.200M KOH (titrating with X remember means X is the titrant).

$$M = \frac{\text{mmol}}{\text{mL}}$$

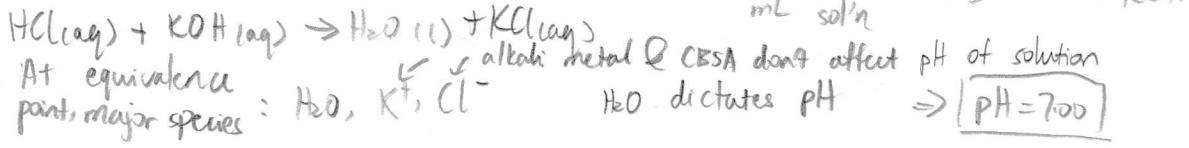
Starting point (starting point = 0 mL of titrant added. Label on graph): consider the starting point of the curve; we have only analyte here: 0.100 M HCl. Calculating the pH of a strong acid is a skill you already have.

$$\boxed{\text{pH} = 1.000} \quad \text{for } 0.100 \text{ M HCl}$$

Equivalence point (Label on graph): The next important point on the curve is the **equivalence point**. (equivalence point = neutralization point = stoichiometric point). The moles of titrant = moles of analyte at the equivalence point. What volume of KOH has one added for this problem? What are my major species at this point?

At equivalence point
what volume of KOH
has been added?

$$30.0 \text{ mL} \times \frac{0.100 \text{ mmol HCl}}{\text{mL sol'n}} = 3.0 \text{ mmol HCl}$$



Note how the curve is quite steep around the equivalence point. The steepness results since when the analyte is nearly all used up, it won't take much titrant to cause the pH to change significantly. The equivalence point is halfway up the steep portion of the curve in a titration.

Post-equivalence point (label on graph): What becomes the major species that will dictate the pH for all points on this titration curve beginning shortly after the equivalence point (for example, after adding 20.0 mL KOH)?

The excess $[OH^-]$ from the titrant will dictate the pH.

Template 2. Strong base-strong acid titration.

Observe the sketch of a titration curve where 30.0 mL of 0.100M KOH is titrated with 0.200 M HCl.

This titration requires a reverse logic of template 1. Let's see if you've got it...

Starting point. What dictates the pH with 0 mL of titrant added?

0.100 KOH; $[OH^-]$ from KOH that dictates the pH
and therefore also the pH.

What's the volume of titrant added at the equivalence point? What will be major species, dictating the pH at this point? 15.00 mL of titrant added $KOH(aq) + HCl(aq) \rightarrow KCl(aq) + H_2O(l)$
major species. H_2O , K^+ , Cl^-

These don't affect the pH of solution

For all points on the titration curve starting shortly after the equivalence point, what dictates the pH? $[H^+]$ from excess point

Template 3. Titration of a Weak Acid with a Strong Base

Problem: Calculate the pH in the titration of 20. mL of 0.10M $HC_7H_5O_2$ with NaOH (0.100 M) after the addition of a) 0 mL NaOH b) 10.0 mL NaOH c) 20.0 mL NaOH d) 30.0 mL NaOH.

($K_a(HC_7H_5O_2) = 6.4 \times 10^{-5}$; $HC_7H_5O_2$ = benzoic acid)

(Remember: 0.10 M NaOH \rightarrow 0.10 M Na^+ and 0.10 M OH^-) Dissociate strong acids/ionic compounds first.

- At the starting point of the titration (0 mL titrant added), one has 0.10 M $HC_7H_5O_2$ present, a weak acid. You learned earlier in the course how to calculate the pH of a weak acid solution.

pH = 2.60 for 0.10 M (seen this calculation in Chapter 14, Zumdahl)

- b) After adding 10.0 mL NaOH to our benzoic acid solution, you have reached what is called the **halfway point**. (Label on graph.) halfway point = half-equivalence point = half the volume of titrant required to reach the equivalence point has been added

The halfway point is a **very important point** in this titration; let's see why! So, remember our strong base reacts completely with our acid. Note that the amount of titrant in "Before Large K reaction" refers to the moles of titrant for the volume in question before that volume is added. Millimoles are easy to work with since multiplying volume in mL times molarity gives millimoles: $20.0 \text{ mL} \times 0.10 \text{ M HC}_7\text{H}_5\text{O}_2 = 2.0 \text{ mmol HC}_7\text{H}_5\text{O}_2$ and $10.0 \text{ mL} \times 0.10 \text{ M OH}^- = 1.0 \text{ mmol OH}^-$.

^{benzoic acid}	$\text{HC}_7\text{H}_5\text{O}_2 + \text{OH}^- \rightarrow \text{C}_7\text{H}_5\text{O}_2^-$		
Before Large K reaction	2.0	1.0	0 (mmol)
Change	-1.0	-1.0	+1.0
After Large K reaction	1.0	0	1.0

We see that the one has the same number of mmoles (and consequently the same concentration) of weak acid solute and its conjugate base at the halfway point. Consequently we have an optimal **buffer at the halfway point of a weak acid-strong base titration!**

What is the pH equal to at the halfway point of a weak acid-strong base titration?

$$\text{pH} = \text{pK}_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right)$$

At halfway point for a weak acid
titrated with a strong base
 $\rightarrow \text{pH} = \text{pK}_a$ (of weak acid being titrated)

Important: What seems like a minor, irrelevant point about the halfway point MAY very well cost you dearly on an exam problem if you write it off as a minor, boring fact that you'd rather not think about. The pH at the halfway point MAY BE the ONLY way you'll know the pKa, which may be required to solve other aspects of a given problem.

- c) What point have we reached when 20.0 mL of 0.100M NaOH has been added (Label on graph)? equivalence point (2.0 mmol OH^- are added to reach equivalence point)

Think carefully. What major species is dictating our pH at this point?

	$\text{HC}_7\text{H}_5\text{O}_2 + \text{OH}^- \rightarrow \text{C}_7\text{H}_5\text{O}_2^-$		
Before Large K reaction	2.0	2.0	0 (mmol)
Change	-2.0	-2.0	+2.0
After Large K reaction	0	0	2.0

After large K reaction,

major species: Na^+ , $\text{C}_7\text{H}_5\text{O}_2^-$, H_2O

↑
does not
affect pH

↑
conjugate base
of weak acid being titrated
that dictates the pH, and
makes the solution basic.

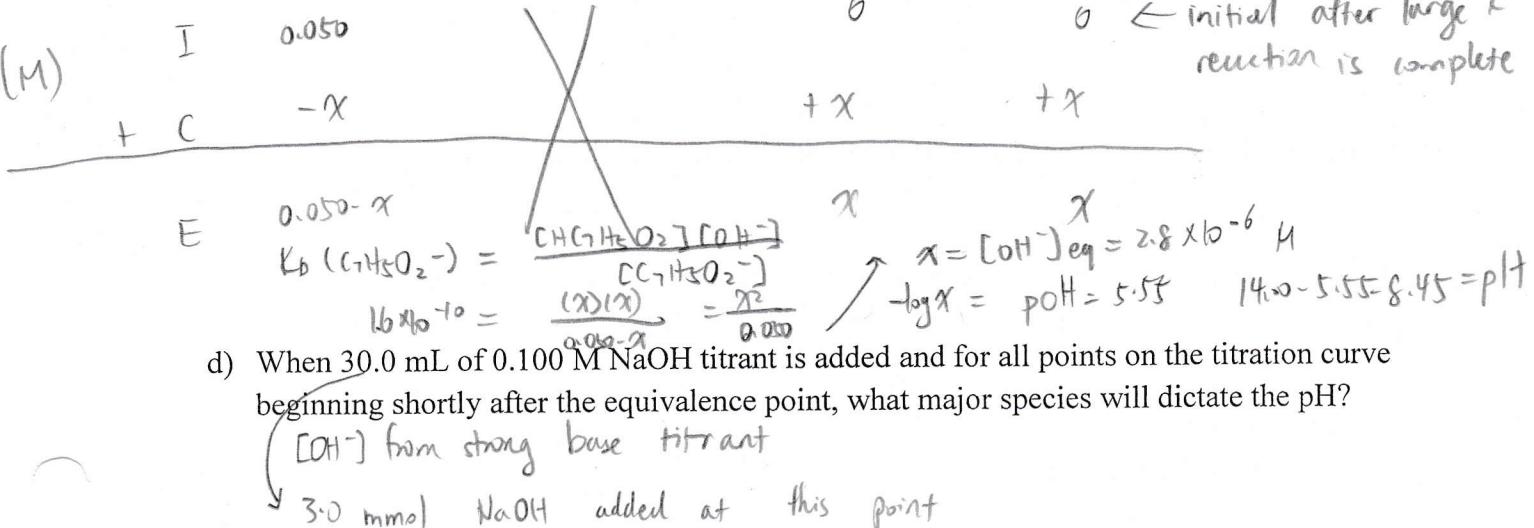
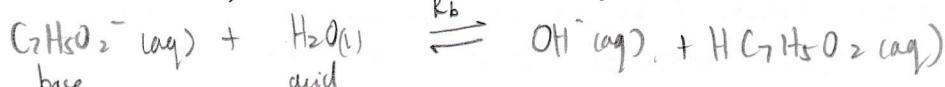
$$\frac{2.0 \text{ mmol } C_7H_5O_2^-}{40.0 \text{ mL}} = 0.050 \text{ M } C_7H_5O_2^-$$

Is the pH neutral, basic or acidic at the neutralization point for a weak acid-strong base titration?

$$\underline{\text{basic}} \quad \underline{K_w} = K_b(C_7H_5O_2^-) \quad \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-5}} = 1.6 \times 10^{-10}$$

$$K_a(HC_7H_5O_2)$$

Show the calculation required to determine the pH of the solution at this point (do not forget to consider the total volume, which is the volume of analyte solution plus that of titrant added!).



Calculate the pH of the solution. Think about how little $[OH^-]$ was produced from the conjugate base of the weak acid at the equivalence point and how this amount is negligible compared to the $[OH^-]$ produced from the excess titrant.

	2.0	3.0	0	(mmol)
Before Large K reaction	2.0	3.0	0	
Change	-2.0	-2.0	+2.0	
After Large K reaction	0	1.0	2.0	

1.0 mmol OH^-

$$\text{total volume} \rightarrow \frac{1.0 \text{ mmol } OH^-}{50.0 \text{ mL}} = 0.020 \text{ M } OH^-$$

$$-\log [OH^-] = pOH$$

$$-\log (0.020 \text{ M}) = 1.70 = pOH$$

Template 4. Titration of a Weak Base with a Strong Acid.

For this section, let's imagine the titration of 20. mL of 0.100M methylamine CH_3NH_2 ($K_b = 4.38 \times 10^{-4}$) with 0.10 M HNO_3 . This is like thinking in the reverse fashion of Template 3 in some ways. Let's see if we've understood the important lessons here.

(Remember: $0.10 \text{ M HNO}_3 \rightarrow 0.10 \text{ M H}^+ + 0.10 \text{ M NO}_3^-$)

At the starting point of the titration, 0.10 M methylamine, a weak base is present (0 mL titrant added). You've already learned how to calculate the pH of a weak base solution. Write the pH below.

$$\boxed{\text{pH} = 11.82}$$

What point will we have reached after 10.0 mL of nitric acid has been added?

What will be true of the amount of weak base solute and its conjugate acid at this point?

	weak base CH_3NH_2	strong acid : L.R. H^+	\rightarrow	CH_3NH_3^+	
Before Large K reaction	2.0	1.0		0	(mmol)
Change	-1.0	-1.0		+1.0	
After Large K reaction	1.0	0		1.0	

M ratio $\text{CH}_3\text{NH}_2 : \text{CH}_3\text{NH}_3^+ = 1:1$ \therefore Good buffer

Calculate the pOH at the halfway point using the Henderson-Hasselbalch equation for pOH since we have a buffered solution at this point.

$$\text{pOH} = \text{pK}_b \text{ (of B)} + \log \left(\frac{[\text{BH}^+]_f}{[\text{B}]_i} \right)$$

B: weak base being titrated

- At halfway point of titration of weak base with strong acid $[\text{BH}^+] = [\text{B}]$
- At halfway point for weak base - strong acid titration:

$$\boxed{\text{pOH} = \text{pK}_b \text{ (of B)}}$$

Note that the **pH= pKa of the conjugate acid of the weak base being titrated** at the halfway point of a weak base-strong acid titration. See the derivation below:

Alternative form of equation 1: $\text{K}_a(\text{BH}^+), \text{K}_b \text{ (of B)} = \text{K}_w$

Remember: Equation 1. $\text{K}_a(\text{HA}) * \text{K}_b(\text{A}^-) = \text{K}_w$ and Equation 2. $\text{pH} + \text{pOH} = 14.00$

Taking the -log of both sides of Equation 1: $-\log \text{K}_a \text{ (for HA)} - \log \text{K}_b \text{ (for A-)} = -\log \text{K}_w$

$$\text{pK}_a \text{ (for HA)} + \text{pK}_b \text{ (for A-)} = \text{pK}_w = 14.00$$

Consequently, if the pK_b (for a weak base) = pOH, then the pK_a (for the weak base's conjugate acid) must be equal to the pH of the solution.

After adding 20. mL of 0.10M HNO₃, what point will have been reached (indicate on graph)?

equivalent point

For a weak base-strong acid titration, what major species will be dictating the pH at the equivalence point? conjugate acid of weak base being titrated

	CH ₃ NH ₂ +	H ⁺ → CH ₃ NH ₃ ⁺	
Before Large K reaction	2.0	2.0	0 (mmol)
Change	-2.0	-2.0	+2.0
After Large K reaction	0	0	2.0

After large K reaction is complete: major species: H₂O, NO₃⁻, CH₃NH₃⁺

So, at the equivalence point of weak base-strong acid titration, will the solution be acidic, basic or neutral? acidic

Calculate the pH (again don't forget to consider the TOTAL volume, titrant solution plus analyte solution).

$$\frac{2.0 \text{ mmol } \text{CH}_3\text{NH}_3^+}{40 \text{ mL}} = 0.050 \text{ M } \text{CH}_3\text{NH}_3^+$$

$$K_a(\text{CH}_3\text{NH}_3^+) = \frac{K_w}{K_b(\text{CH}_3\text{NH}_3^+)} = \frac{1.0 \cdot 10^{-14}}{4.38 \cdot 10^{-4}} = 2.28 \cdot 10^{-11}$$



(M)	I	0.050	X	0	0
	C	-x	X	+x	+x
	E	0.050-x	X	x	x

$$K_a = \frac{[\text{CH}_3\text{NH}_2^{\text{eq}}][\text{H}_3\text{O}^{\text{eq}}]}{[\text{CH}_3\text{NH}_3^{\text{eq}}]} = \frac{x \cdot x}{0.050-x} = 2.28 \cdot 10^{-4}$$

$$-\log x = -\log [\text{H}_3\text{O}^{\text{eq}}]$$

$$\boxed{\text{pH} = 5.97}$$

↑

$$x = 1.07 \cdot 10^{-6} \text{ M}$$

small K approximation

$$0.050-x \approx 0.050$$

Is there a good buffer at the equivalence point?

No, we have $\approx 0.050 \text{ M } \text{CH}_3\text{NH}_3^+$ and $1.07 \cdot 10^{-6} \text{ M } \text{CH}_3\text{NH}_2$

⇒ We do not have similar amount of weak base & its conjugate acid.

For all points on the titration curve beginning shortly after the equivalence point, for example, after adding 25.0 mL of 0.100M HNO₃, what major species will be dictating the pH of the solution? (indicate on graph)

[H⁺] from excess strong acid titrant.

See figure 15.8 in Zumdahl to see many indicator
Indicators: Learning How to Pick the Correct Indicator for a Given Titration

An indicator changes colour at what is known as the **endpoint**. For an indicator to be effective, one wants the volume of titrant required to reach the endpoint to be as close as possible to the volume of titrant required to reach the equivalence point.

For phenolphthalein In^- is pink, HIn is colorless

The indicator is often a weak acid, which is often written as HIn . ($K_{\text{in}} = K_a$ for an indicator). The deprotonated form of an indicator (In^-) has one colour, while the protonated form (HIn) of an indicator has a second colour. Adding OH^- to an acidic solution, an indicator is seen to change colour when the $[\text{In}^-]/[\text{HIn}]$ ratio is roughly 1/10. If, on the other hand, one is adding H^+ to a basic solution, an indicator is seen to change colour when the $[\text{In}^-]/[\text{HIn}]$ ratio is roughly 10/1.

$$\log \left(\frac{1}{10}\right) = -1 \quad \log \left(\frac{10}{1}\right) = +1$$

When picking an appropriate indicator, one looks at an indicator's pK_a value. Remembering that the pH (of solution with indicator) = pK_a (indicator) + $\log ([\text{In}^-]/[\text{HIn}])$, the pH (colour change of indicator) = pK_a (indicator) - 1 when one is adding base to an acidic solution and the pH (colour change of indicator) = pK_a (indicator) + 1 when one is adding acid to a basic solution.

When picking an indicator, one looks for the indicator where the pH of the equivalence point is closest to the pH of the colour change of the indicator. However, in practice, as long as the volume needed to reach the pH at the equivalence point is the same as the volume required for the indicator to change colour, an indicator is a good choice.

What type of weak acid do you think your indicator might be if it undergoes two colour changes, one at a lower pH and the second at a higher pH ? Some indicators are polyprotic acids, H_2In has one color, HIn^- has a second color, In^{2-} has a third color.

Question: Imagine phenol red in acidic solution, at what pH will the colour change take place when adding base to the solution? ($K_a(\text{phenol red}) = 1.3 \times 10^{-8}$) \rightarrow phenol red is an indicator

$$\text{pH (of color change)} = pK_a (\text{of phenol red}) - 1$$

$$= -\log (1.3 \times 10^{-8}) - 1 = 6.89 \text{ (first trace of permanent orange)}$$

Question: For phenol red in basic solution, at what pH will the colour change take place when adding acid to the solution?

$$\text{pH (of color change)} = pK_a (\text{of phenol red}) + 1 = 8.89 \text{ (first trace of permanent orange)}$$

If phenol red is yellow at more acidic pH s and red at more basic pH s, under what pH values will phenol red be orange? (Figure 15.8 of Zumdahl has indicators and colour changes.)

From $\text{pH } 6.89$ to 8.89 , the solution is orange with phenol red in it.

Look at the titration curves and decide if phenol red would be a good choice of indicator.

End of
Chapter 15.

Chapter 17 Section 7-9 (Zumdahl textbook)

Lecture Concepts 18. Relating Free Energy to Reaction Quotient and Equilibrium Constants

In this section, we work toward two equations: $\Delta G = \Delta G^\circ + RT\ln Q$ and $\Delta G^\circ = -RT\ln K$, equations that relate free energy change to reaction quotient and equilibrium constant. Note: The Q and the K in the equations in this paragraph are what are described as **thermodynamic Q** and **thermodynamic K**.

To derive the equations in the previous paragraph, we're going to relate free energy to pressure. For simplicity, I'm deriving the equations in the previous paragraph using gases, but one can use a similar derivation to obtain these equations for reactions with aqueous solutes.

To work on developing your logic for what may seem a mysterious equation, we're going to look first at entropy of the system. Place a less than or greater than arrow as appropriate between the two entropies (S) values below for a system of gases.

$S_{\text{high volume}} > S_{\text{low volume}}$ OK, now remember Boyle's Law (n, T constant)

$S_{\text{high pressure}} < S_{\text{low pressure}}$

Temperature (in K) is a positive number

So, given that the entropy of the system is increasing going toward lower pressure conditions, then since the equation $G = H - TS$ is true, the free energy is decreasing (becoming more negative) moving toward lower pressure conditions.

The relationship between free energy and pressure can be expressed by the mathematical expression written on the next line: $\ln(1) = 0$

$$G = G^\circ + RT\ln P$$

where G° is the standard free energy with gases at 1 atm, G is the free energy at some pressure P (atm), R is the universal gas constant 8.314 J/K*mol and T is temp (in Kelvin).

We will NOT be using the equation $G = G^\circ + RT\ln P$ in problems, but it will be used to derive the equations in the first paragraph on this page that we WILL use in problems.

Think: What will be true about G if P=1 atm? $G = G^\circ$

Will free energy be higher or lower relative to the standard state if $P > 1$ atm (think R and T are positive values, and the $\ln P$ is positive when $P > 1$)? $G > G^\circ$ (higher)

Will the free energy be higher or lower relative to the standard state if $P < 1$ atm (remind yourself that the $\ln P$ is negative when $P < 1$)? $G < G^\circ$

OK, so from the equation $G = G^\circ + RT\ln P$ we see that ΔG is becoming more positive as the pressure increases, which jibes well with the fact that the entropy of a system of gases decreases moving toward higher pressure. But where did this equation come from??

$G = G^\circ + RT \ln P$ actually simply comes from a mathematical manipulation of the equation $G = H - TS$, the definition of free energy! Unfortunately, this math requires a knowledge of a full year of calculus which not all students have had. As a result, I will not derive the equation during class time but I write the derivation in italics, if you're interested.

So, by definition $G = H - TS$, yes? And $H = E + PV$, yes?

Therefore, $G = E + PV - TS$. If we look at small changes, $dG = dE + d(PV) - d(TS)$
 $dE = q_{rev} + w_{rev}$; $w_{rev} = -pdV$ and if you look back to the section in italics: Lecture Concepts. Intro to Spontaneity and Entropy, you'll find the derivation of the expression $q_{rev} = TdS$. The q_{rev} and w_{rev} refer to small changes in work and heat.

So, $dG = TdS - pdV + d(PV) - d(TS)$. Here the chain rule has been applied to the $d(PV)$ and $d(TS)$ part.

Then you get, $dG = Tds - pdV + pdV + VdP - TdS - SdT$; some parts cancel out giving you:
 $dG = VdP - SdT$

Since we're looking AT a given temperature, $dT = 0$, so therefore,
 $dG = VdP$; rearranging this expression from Ideal Gas Law $dG = nRT/PdP$

If we then do a definite integral (left side of math equation, from G° to G (at some pressure P), right side of math equation consequently is from 1 atm to some pressure P), then:
 $G - G^\circ = nRT \ln P / 1$, so for 1 mole, $G = G^\circ + RT \ln P$. Voilà.

$G = G^\circ + RT \ln P$ is not used in problems itself, but allows us to derive several equations that will be useful in problems

Determining spontaneity at non-standard state conditions

We learned in an earlier section several ways to calculate the ΔG° values, when reactants and products are under standard state conditions. That's great, but what if there are non-standard state values of our system's reactants and products present? How does one know if the reaction will proceed in the forward direction under non-standard-state conditions?

Now, remember: in a reaction what we're interested in is ΔG , to see if a reaction is spontaneous or not. On the next page, an equation is derived that shows how to determine ΔG for a reaction that will work for non-standard-state conditions (as well as standard-state conditions) using thermodynamics data.

Consider a random reaction $A(g) + 2B(g) \rightarrow C(g)$.

For G_A° , I might say "Gee-A-Nought"

(vocabulary: G_A = free energy of gas A, G_A° = free energy of gas A under standard state conditions, P_A = pressure of A (in atm))

For the random reaction above, by definition:

First equation

Last three equations

$$\Delta G = G_C - (2G_B + G_A); \quad G_A = G_A^\circ + RT\ln P_A; \quad G_B = G_B^\circ + RT\ln P_B; \quad G_C = G_C^\circ + RT\ln P_C$$

Substituting the last three equations into the first equation on the previous line, one gets the following equation:

$$\Delta G = G_C^\circ + RT\ln P_C - (2(G_B^\circ + RT\ln P_B) + G_A^\circ + RT\ln P_A)$$

$$\Delta G = G_C^\circ - (2G_B^\circ + G_A^\circ) + RT(\ln P_C - (2\ln P_B + \ln P_A)) \leftarrow \text{the above equation rearranged}$$

$$\Delta G = G_C^\circ - \underbrace{(2G_B^\circ + G_A^\circ)}_{\Delta G^\circ} + RT(\ln(P_C/P_B^2 * P_A)) \leftarrow \text{above equation rearranged, doing logarithmic math}$$

Re-express the equation above in the form that will be useful to you for problems:

$$\boxed{\Delta G = \Delta G^\circ + RT \ln Q_{th}}$$

*use equation to find
the ΔG for reaction
when one has non-standard
state pressures + concentrations*

Q = reaction quotient

What does Q_{th} stand for, and when do you use it? (units of R and T if ΔG s in Joules?)

*Q_{th} = thermodynamic Q one only uses Q_{th} when using this
equation or when using equations
derived from the equation.*

$Q_{th} = Q_p$ ← $Q_{th} = Q_p$ for a system of only gases; $Q_{th} = Q_c$ for a system of only aqueous solutes; for a mixture of gases and aqueous solutes, the Q_{th} is reaction quotient made by taking mathematical product of all reaction products to the power of their coefficient in the numerator divided by the mathematical product of all reactants to the power of their coefficient in the denominator such that aqueous solutes are in units of molarity and the gases are in units of atm.
*(if one has
gases only in
addition to
liquids &
solids in an
equation)*

What is Q_{th} for $Cu(s) + 2H^+(aq) \rightarrow H_2(g) + Cu^{2+}(aq)$

$$Q_{th} = \frac{P_{H_2} \cdot [Cu^{2+}]}{[H^+]^2}$$

*P_{H_2} = pressure of
 H_2 (in atm)*

Problem:

Given the following partial pressures of gases in a reaction vessel: $P_{\text{hydrogen sulfide}} = 1.0 \times 10^{-4} \text{ atm}$, $P_{\text{sulfur dioxide}} = 1.0 \times 10^{-2} \text{ atm}$ and $P_{\text{water}} = 3.0 \times 10^{-2} \text{ atm}$ and that the standard free energies of formation are $\Delta G^\circ_f(\text{H}_2\text{S(g)}) = -34 \text{ kJ/mol}$, $\Delta G^\circ_f(\text{SO}_2\text{(g)}) = -300 \text{ kJ/mol}$ and $\Delta G^\circ_f(\text{H}_2\text{O(g)}) = -229 \text{ kJ/mol}$, calculate the ΔG for the reaction below at 25°C. The K_p for this reaction = 6.0×10^{15} .



We're going to use our equation now (but not blindly). $\Delta G = \Delta G^\circ + RT \ln Q_p$

Calculate the value of ΔG° first.

$$Q_p = Q^\circ$$

Why is the value of ΔG° not good enough to tell us if the forward reaction will be spontaneous given the partial pressures listed. ΔG° tells you that the forward reaction is spontaneous if each of the gaseous reactants and products has a pressure of what? 1 atm pressure of both reactants & products

Now solve for Q and then ΔG .

$$\Delta G^\circ = \sum n_p \Delta G^\circ_f(p) - \sum n_r \Delta G^\circ_f(r)$$

$$\Delta G^\circ = [3 \cdot \Delta G^\circ_f(\text{S}) + 2 \Delta G^\circ_f(\text{H}_2\text{O})] - [2 \cdot \Delta G^\circ_f(\text{H}_2\text{S}) + 1 \cdot \Delta G^\circ_f(\text{SO}_2)]$$

$$\Delta G^\circ = [3 \cdot 0 \text{ kJ/mol} + 2 \cdot -229 \text{ kJ/mol}] - [2 \cdot -34 \text{ kJ/mol} + 1 \cdot -300 \text{ kJ/mol}]$$

$$\Delta G^\circ = -90 \text{ kJ/mol}$$

$$Q_p = \frac{P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2\text{S}} \cdot P_{\text{SO}_2}} = \frac{(3.0 \times 10^{-2} \text{ atm})^2}{(1.0 \times 10^{-4} \text{ atm})^2 (1.0 \times 10^{-2} \text{ atm})} = 9.0 \times 10^6$$

$$\Delta G = \Delta G^\circ + RT \ln Q_p$$

$$\Delta G = -90 \text{ kJ/mol} + 0.008314 \frac{\text{J}}{\text{K} \cdot \text{mol}} \cdot 298 \text{ K} \cdot \ln(9.0 \times 10^6)$$

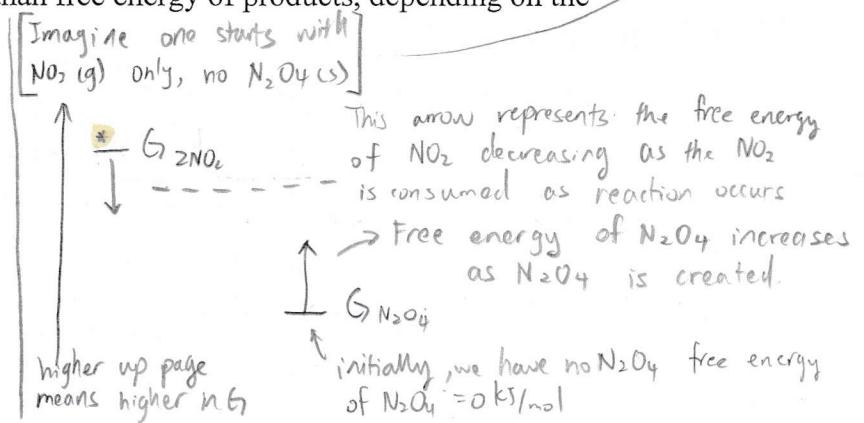
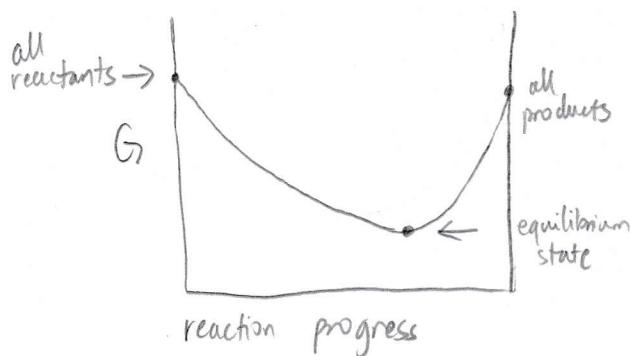
$$\boxed{\Delta G = -50 \text{ kJ/mol}} \leftarrow \text{change in free energy given the initial pressures mentioned in problem}$$

Note a way of double-checking your answer for a problem using the equation $\Delta G = \Delta G^\circ + RT \ln Q$. $Q_p < K_p$, which remember means that the reaction proceeds to the right, in the forward direction, to achieve equilibrium. So if $Q_p < K_p$, then the reaction proceeds spontaneously, so must have a negative value of ΔG . (Similarly if $Q_p > K_p$, the reaction must have a positive value of ΔG , since the reverse of the reaction written will proceed spontaneously in this case.)

Remember that a reaction will occur spontaneously until it reaches the equilibrium state.

Think: A reaction occurs until it reaches the lowest possible free energy value. This value must be the equilibrium state, since ΔG is negative for a reaction occurring spontaneously.

Plot free energy vs. reaction progress. Place 3 energy levels: all reactants, all products and the equilibrium state (mixture of reactants and products) on the graph. I'm choosing arbitrarily to have all reactants higher in free energy than all products and I'm picking a random point for the equilibrium state (the equilibrium state could be much closer to all reactants or all products, and the free energy of reactants could be lower than free energy of products, depending on the reaction).



We've seen that free energy increases with increasing pressures (also concentrations) by the equation $G = G^\circ + RT \ln P$.

Let's consider $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$; as the reaction proceeds G for 2NO_2 decreases and G for N_2O_4 increases. (Put a free energy diagram with one energy level for NO_2 and the second for N_2O_4 , with arrows showing one increasing and the other decreasing; then make a second diagram indicating that they must be equal at one point.)

If $\Delta G = 0$ (note G not G°), then at this point the reaction is spontaneous in neither direction ($G_{\text{products}} = G_{\text{reactants}}$). What state have we reached now?

equilibrium state

Q_p (or Q_{th} for gases) is equal to what at this point?

Take the equation $\Delta G = \Delta G^\circ + RT \ln Q_{\text{th}}$ and make the substitutions to make a critical equation in problems (place in box with stars):

$$\text{At equilibrium } \Delta G = 0 \quad Q_{\text{th}} = K_{\text{th}}$$

$$0 = \Delta G^\circ + RT \ln (K_{\text{th}}) \Leftrightarrow \boxed{\Delta G^\circ = -RT \ln (K_{\text{th}})} \rightarrow \text{Powerful equation}$$

What are the units of R and T in the equation $\Delta G^\circ = -RT \ln K_{\text{th}}$ (if ΔG° is in Joules)? K_{th} = thermodynamic K

Or if one only has gases
in addition to liquids and solids

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If all species in a reaction are gases, $K_{th} = K_p$; if all species in a reaction are aqueous solutes, $K_{th} = K_c$. If one has a mixture of gases and solutes, the K_{th} is made by taking mathematical product of all reaction products to the power of their coefficient in the numerator divided by the mathematical product of all reactants to the power of their coefficient in the denominator such that aqueous solutes are at equilibrium in units of molarity and the gases are at equilibrium in units of atm.

This is an incredibly powerful equation in thermodynamics as it allows one calculate the free energy from the equilibrium constant and vice versa!!!! $\ln(1) = 0$

If ΔG° is...	Then K_{th} is...	In which direction do reactions under standard state conditions occur to achieve equilibrium?
=0		under standard state conditions reaction is at equilibrium
<0	>	relative to standard state, reaction proceeds to right to reach equilibrium
>0	<	relative to standard state, reaction proceeds to left to achieve equilibrium

\ln of a $k > 1$ gives a positive value; \ln of $k < 1$ gives a negative value

The equation $\Delta G^\circ = -RT\ln K_{th}$ gives us an additional method in this course to determine ΔG° (keep track of all the different methods to do this)! From experimental data for an equilibrium constant, a ΔG° value can be calculated. Similarly, from ΔG°_f tables (and other thermodynamic data that lead to the ΔG°_{rxn}), K values can be calculated.

Problem: From standard Gibbs free energies of formation, calculate the value of K_p for the reaction $3\text{NO(g)} \rightleftharpoons \text{N}_2\text{O(g)} + \text{NO}_2\text{(g)}$ at 25°C. From tables of standard free energies of formation, $\Delta G^\circ_f(\text{NO})$: 87 kJ/mol, and $\Delta G^\circ_f(\text{NO}_2)$: 52 kJ/mol and $\Delta G^\circ_f(\text{N}_2\text{O})$: 104 kJ/mol.

(The ΔG° value in $\Delta G^\circ = -RT\ln K_{th}$ refers to one mole of reaction as written.)

$$\Delta G^\circ = [\Delta G^\circ_f(\text{N}_2\text{O}) + \Delta G^\circ_f(\text{NO}_2)] - [3 \cdot \Delta G^\circ_f(\text{NO})]$$

$$[104 \text{ kJ/mol} + 52 \text{ kJ/mol}] - [3 \cdot 87 \text{ kJ/mol}]$$

$$\Delta G^\circ = -105 \text{ kJ/mol} = -RT \cdot \ln K_{th} \quad K_{th} = K_p \text{ (all gases)}$$

$$-105 \text{ kJ/mol} = -0.008314 \frac{\text{kJ}}{\text{K mol}} \cdot 298 \text{ K} \cdot \ln K_{th}$$

$$e^{42.4} = e^{\ln K_{th}}$$

$$K_{th} = K_p = 254 \times 10^{18}$$

Double-check your answer. Does it make sense? If we have a very large K , would we expect this to correspond to a positive or negative ΔG° ? negative ΔG° , it makes sense

Lecture Concepts 19. Temperature Dependence of K and Another Way of Thinking About Change in Free Energy

So, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and $\Delta G^\circ = -RT\ln K_{th}$, so therefore $-RT\ln K_{th} = \Delta H^\circ - T\Delta S^\circ$

Multiply both sides of this latter equation by $-1/RT$ to make a new equation... then make an equation for a line from this equation. Experimentally $= \ln K_{th} \text{ vs. } \frac{1}{T}$ gives a line observed

$$\ln K_{th} = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$$

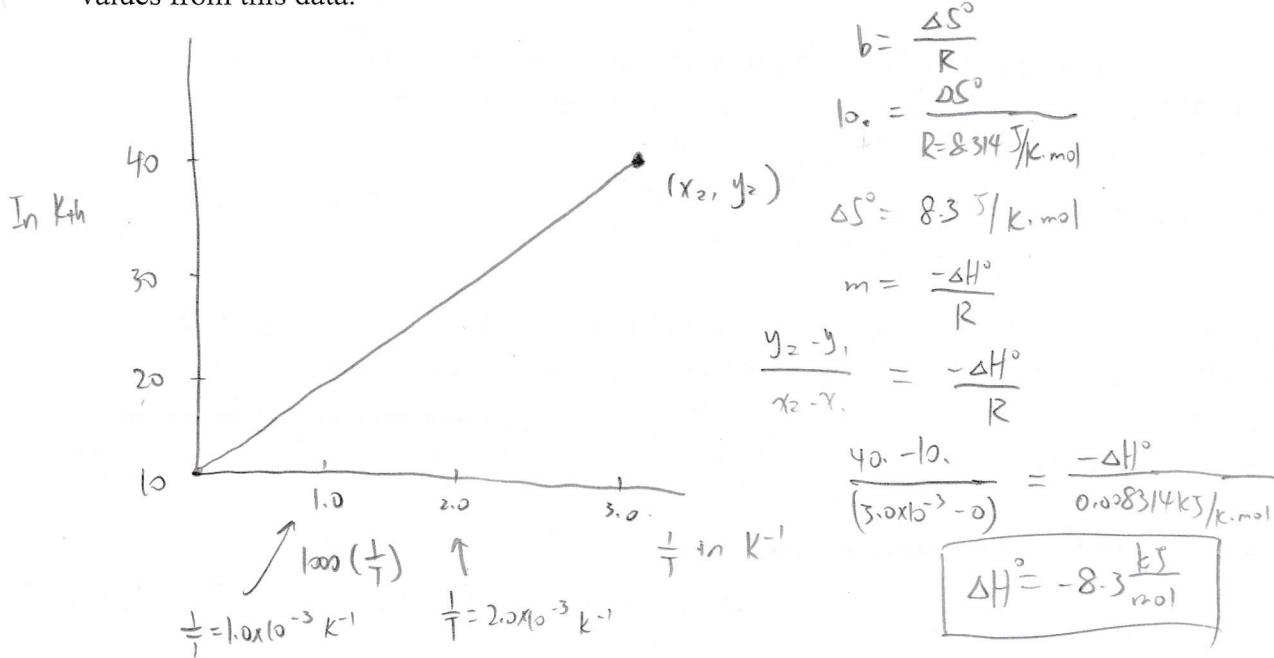
$y = m x + b$

$m = \text{slope}$
 $b = y\text{-intercept}$

\leftarrow Equation in box is one form of the Van't Hoff equation

The sign of the slope of the line for $\ln K$ vs $1/T$ consequently is positive if the reaction is exothermic. The sign of the slope of the line for $\ln K$ vs. $1/T$ is negative if the reaction is endothermic. The signs of these slopes agree with what we observed from Le Chatelier's Principle that endothermic reactions go more effectively (so have larger K) at higher temperatures and that exothermic reactions go more effectively at lower temperatures.

Make a plot of $\ln K$ vs. $1000(1/T)$ (K^{-1}), a straight line increasing starting with $\ln K = 10$. going to $\ln K = 40$. and $1/T$ from 0 to $3.0 \times 10^{-3} K^{-1}$ (data is extrapolated). Calculate the ΔH° and ΔS° values from this data.



This graphical approach gives us yet another means to calculate ΔH° and ΔS° from experimental data

$$\ln K_{th} = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R} \rightarrow \text{van't Hoff equation}$$

$$y = m x + b$$

So, for a given reaction

$$\ln K_1 + \Delta H^\circ / R (1/T_1) = \ln K_2 + \Delta H^\circ / R (1/T_2) = \Delta S^\circ / R,$$

where K_1 is the (thermodynamic) equilibrium constant at T_1 (T_1 = temperature 1) and K_2 is the (thermodynamic) equilibrium constant at T_2 (T_2 = temperature 2). For such an equation, we'll make the approximation that the thermodynamic function ΔH° and does not vary appreciably over the temperature range examined; $\Delta S^\circ / R$ can be taken as the y-intercept for the plot of $\ln K$ vs. $1/T$.

Rearrange the first two equations to give the **van't Hoff equation**, a useful expression to calculate the equilibrium constant for a given reaction at one temperature if the equilibrium constant at a second temperature is known.

$$\ln K_1 - \ln K_2 = \boxed{\ln \left(\frac{K_1}{K_2} \right) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)} \rightarrow \text{another form of van't Hoff equation}$$

This expression can be used to calculate the vapour pressure at one temperature from the vapour pressure at another temperature: consider a vaporization of $A(l) \rightleftharpoons A(g)$ (where A is some element or compound), what is the equilibrium constant K_{th} equal to?

Since there are only gases in vaporizations equilibrium constant $K_{th} = K_p = P_A = \text{vapor pressure of } A \text{ (in atm)}$

With this knowledge, we get the **Clausius-Clapeyron equation** (write below), that is a mathematical representation of the logarithmic increase of vapour pressure with temperature. (P_1 = vapour pressure at T_1 , P_2 =vapour pressure at T_2)

$$\boxed{\ln \left(\frac{P_1}{P_2} \right) = \frac{\Delta H^\circ \text{ vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)} \rightarrow \text{Clausius-Clapeyron equation}$$

Problems with this equation are found in Chapter 10 of Zumdahl

since this Problem (van't Hoff): Hydrazine, N_2H_4 , has a normal boiling point of $113.5^\circ C$ and a critical point at $380.0^\circ C$ and 145.4 atm . Calculate the heat of vaporization for hydrazine (in kJ/mol).

\rightarrow Normal boiling point is the boiling point when external pressure = 1 atm

-boiling point is the temperature at which vapor pressure of above $\hookrightarrow 1 \text{ atm}$

a liquid = external pressure

has \propto s.t.

\rightarrow Critical point is at the end of boiling point curve on a phase diagram.

$$113.5^\circ C = 386.65 K$$

$$380.0^\circ C = 653.15 K$$

$$R = 0.008314 \text{ kJ/K.mol}$$

$$\ln \left(\frac{145.4 \text{ atm}}{1 \text{ atm}} \right) = \frac{\Delta H^\circ}{0.008314 \text{ kJ/K.mol}} \left(\frac{1}{653.15 \text{ K}} - \frac{1}{386.65 \text{ K}} \right)$$

$$\boxed{\Delta H^\circ \text{ vap} = 39.24 \text{ kJ/mol}}$$

\hookrightarrow One must have a positive a positive value for heat of vaporization.

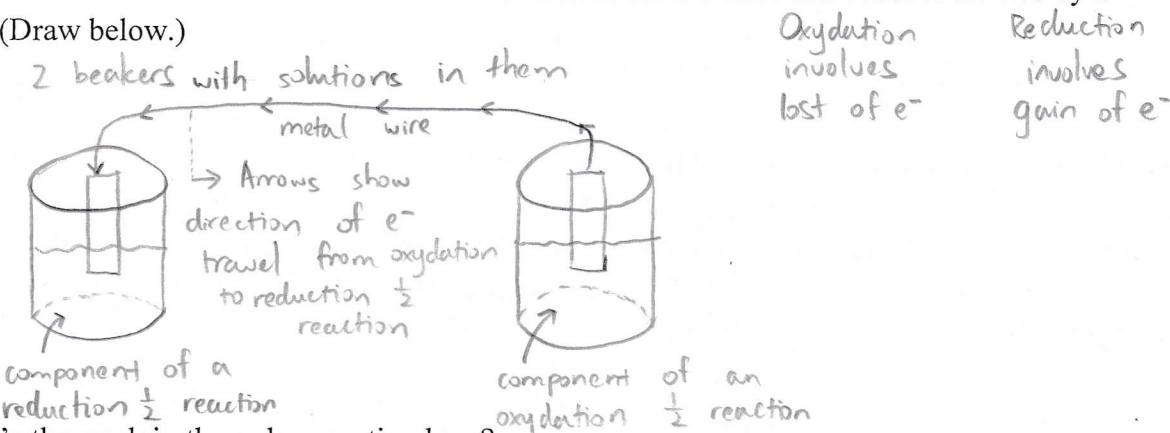
Free Energy and Electrical Work Chap. 17 section 9

Derivation: As we learned in the beginning, $\Delta E = q + w$

→ ONLY CASE where you ran across electrical work is when a redox reaction is occurring.

So far, we've learned about PV work, compression & expansion of gases, but there's also **electrical work**. Sometimes electrical work is called "**useful work**", which strikes me as a little silly of a name since PV work is hardly useless....but anyhow...pet peeve there....

This is a bit of foreshadowing to the final section of this course (electrochemistry); to get a bit of a sense of what "electrical work" is...imagine you have the components of an oxidation $\frac{1}{2}$ reaction in one beaker and a reduction $\frac{1}{2}$ reaction in another beaker and connect the two by a wire. (Draw below.)



Where's the work in the redox reaction here?

The electrical work is the work associated with electrons traveling through wire

Now, I'm going to do a derivation for you (not responsible for derivation in italics) to show what "useful work" is equal to at constant pressure (how redox reactions are often done):

$$\Delta E = q_p + w_{PV} + w_{useful} \text{ (note: all I've done is divide work into "useful work" and PV work.)}$$

$$\Delta H - P\Delta V = q_p - P\Delta V + w_{useful}$$

As we learned earlier, $\Delta H = \Delta E + P\Delta V$, so therefore, plugging into the previous equation,

$$\Delta H = q_p + w_{useful} \text{ (dH= small changes in H)}$$

Now, if we go back to the section *Lecture Concepts. Intro to Spontaneity and Entropy*, you'll find the derivation of the expression for small changes in heat: $q_{rev} = TdS$. So, looking at small changes of: $dH = TdS + w_{useful}$, so what you think "useful work" is equal to?

$$w_{useful} = dH - TdS \leftarrow \text{small changes in useful work}$$

$$\Delta G = w_{useful} = \Delta H - T\Delta S \leftarrow \text{large changes in useful work}$$

However, the change in **free energy** is said to be the maximum work that can be obtained from a redox reaction; not all the free energy is actually free to be used as electrical work. Why?

Some of free energy can be lost due to frictional heating as electrons travel through wire.

For this reason, it is sometimes written that

$$\Delta G = w_{max}$$

w_{max} = maximum useful work (assuming no energy loss from frictional heating in wire)

Chapter 12 - Zumdahl Textbook

Lecture Concepts 20. Introduction to Kinetics.

Chemical kinetics is the branch of chemistry that looks at what?

reaction rates

Why do we care about kinetics in addition to spontaneity and free energy?

One reason is that one is interested not only in whether reactions can occur but also in how quickly they can occur.

Reaction rate = change in concentration of a reactant or product per unit time

$$\text{Rate of reaction} = \frac{\Delta[\text{Product}]}{\Delta t} \quad \text{or} \quad -\frac{\Delta[\text{Reactant}]}{\Delta t}$$

$$\Delta t = \text{time final} - \text{time initial}$$

Why is there a minus sign in front of $\Delta[\text{Reactant}]$? Remember rates are **ALWAYS** positive.

→ Remember: $[\text{Reactant}]_{\text{final}} < [\text{Reactant}]_{\text{initial}}$

Problem: Consider the decomposition of an aqueous solution of H_2O_2 at a given temperature. If one starts with 1.000M H_2O_2 and 20.0s later the solution is 0.966 M H_2O_2 , what is the rate of hydrogen peroxide consumption over that period of time?

$$\text{Rate of reaction} = \frac{-\Delta[\text{H}_2\text{O}_2]}{\Delta t} = \frac{-(0.966 \text{ M} - 1.000 \text{ M})}{20.0 \text{ s}} = 1.7 \cdot 10^{-3} \text{ M/s}$$

Consider the reaction $\text{H}_2(\text{g}) + 2\text{ICl}(\text{g}) \rightarrow \text{I}_2(\text{g}) + 2\text{HCl}(\text{g})$.

So, over a given period of time, for every unit of hydrogen gas that reacts, two units of iodine monochloride react, one unit of iodine gas is formed and two units of hydrogen chloride are formed.

We often define the rate of reaction in terms of reactant loss or consumption or in terms of product formation. So, therefore the rate of H_2 consumption = $x \cdot (\text{rate of ICl consumption})$ = rate of I_2 production = $x \cdot (\text{rate of HCl production})$. What is $x = ?$ $x = \frac{1}{2}$

So, clearly, when we talk about rates, it is important to specify which reactant being consumed or which product is being formed.

One can measure the rate over a given time interval or one can measure the rate at a given time t. The rate at a given time t = instantaneous rate.

What is the instantaneous rate equal to at time t=x s? The instantaneous rate = the absolute value of **the slope of the tangent to the curve** at time t= x s. While the rate over a given time interval might be described in terms of $-\Delta[\text{Reactant}]/\Delta t$, from calculus when one writes the instantaneous rate at a given time t, one substitutes "d" for " Δ ", so the instantaneous rate might be described as $-d[\text{Reactant}]/dt$.

Consider the graph below for the reaction $\text{H}_2(\text{g}) + 2\text{ICl}(\text{g}) \rightarrow \text{I}_2(\text{g}) + 2\text{HCl}(\text{g})$.

Calculate the instantaneous rate using the slope of the tangent to the curve that the teacher gives you.

$$\left| \begin{array}{l} \text{slope of tangent} \\ \text{to curve at} \\ \text{time } t=2\text{s} \end{array} \right| = |m| = \left| \frac{y_2 - y_1}{x_2 - x_1} \right| = \left| \frac{0.300\text{M} - 0.600\text{M}}{3.95\text{s} - 1.15\text{s}} \right| = 0.107\text{M/s} \\ = -\frac{d[\text{H}_2]}{dt}$$

Initial rate = the absolute value of slope of the tangent to the curve at time t= 0s

Why do you think in kinetics one is often interested in the initial rate? Think: What does one not have to worry about with the initial rate? The rate of reaction only depends on what?

For the initial rate, one does not have to worry about the reverse reaction, since no products have been formed yet. The rate of reaction depends only on the forward direction reaction.

Your textbook (later editions only) 92
 shows instantaneous rates
 using deltas
 e.g. your book shows

$$\frac{-\Delta [A]}{\Delta t} = \frac{-d[A]}{dt}$$

Vocabulary Prior to Doing Method of Initial Rates Problems

Consider a generic reaction: $A + 2B \rightarrow C + 2D$ (A,B,C and D are molecules or atoms)

A rate law = differential rate law = a math equation where the rate of reaction is set equal to the **rate constant k** times the product of the concentration of each reagent to some exponent. The rate law for the generic reaction above could be: rate of reaction = $-d[A]/dt = k[A]^m[B]^n$. The rate law shows how the rate of reaction depends on concentrations of reactants.

The exponent following each reactant is called the order of that reactant. For example, for the rate law above, "m" = The **order** of reactant A. "n" = **order** of reactant B. ☺ BEWARE: Unlike in the law of mass action equilibrium problems, exponents such as m and n won't necessarily be the same as the coefficients. How are m and n determined then?

m and n are determined via experiment

(Experiment seen later today & next week)

The sum of the exponents in a rate law is described as the overall order of reaction

If the sum of the exponents in a rate law = 0, we say the reaction is zeroth order overall; if the sum of the exponents = 1, reaction is first order overall; if the sum of the exponents = 2, the reaction is second order overall. Reactions are most commonly zeroth, first or second order overall. Occasionally however, the overall order of a reaction may be another integer or a fraction.

The rate constant k (note lower case, which distinguishes k from an equilibrium constant) is determined experimentally.

For the reaction $A + 2B \rightarrow C + 2D$, one could write the rate law as: $-d[A]/dt = k[A]^m[B]^n$, but one could also write the rate law as: $-d[B]/dt = k'[A]^m[B]^n$ (k' is also a rate constant).

Remember, "m" and "n" remain the same regardless of whether you're looking at $-d[A]/dt$ or $d[B]/dt$. Write a mathematical equation to relate k to k'

$$2 \cdot k = k'$$

Write the differential rate law for the consumption of A for the reaction $A + 2B \rightarrow C + 2D$ if from experiment, you find that the order of each reactant is "1" and therefore, the overall order of reaction is "2".

$$\text{Rate of reaction} = \frac{-d[A]}{dt} = k[A][B]$$

Lecture Concepts 21. Determining the Form of the Rate Law. Method of Initial Rates and Integrated Rate Law.

So, the order of each reactant must be determined from experiment. Now, we will learn one way by which the orders may be determined called the **method of initial rates**.

Method of initial rates. By this technique, one collects data for the initial rate using a variety of starting initial concentrations; this allows one to determine the orders for the forward reaction as written. (Remind yourself why "initial" is important.)

↳ No reverse reaction is occurring

Let's learn how this is done by considering a specific example.

Problem: For the reaction $2\text{NO(g)} + 2\text{H}_2\text{(g)} \rightarrow \text{N}_2\text{(g)} + 2\text{H}_2\text{O(g)}$, write an expression for the rate law (that is, finding a value for k and the order of each reactant) given the following data:

Experiment #	$[\text{NO}]_0$ (M)	$[\text{H}_2]_0$ (M)	Initial rate (M/s)	$\frac{-d[\text{H}_2]}{dt}$
Exp. 1	0.10	0.20	0.0150	
Exp. 2	0.10	0.30	0.0225	
Exp. 3	0.20	0.20	0.0600	

$$\log(y^*) = x \cdot \log y$$

$$\frac{x^n}{y^n} = \left(\frac{x}{y}\right)^n$$

Step 1. One should start by dividing the rate law of the initial rate of one experiment by the rate law for the initial rate of a second experiment, such that in the two experiments, the **concentration of ONE REAGENT is kept constant**. For our purposes, we should look be on the lookout for the most common orders of reactants: zero, one, two.

k and the exponent do not change as the initial concentrations change

$$\frac{\text{Rate of experiment 2}}{\text{Rate of experiment 1}} = \frac{k \cdot [\text{NO}]_0^m \cdot [\text{H}_2]_0^n}{k \cdot [\text{NO}]_0^m \cdot [\text{H}_2]_0^n} = \frac{k(0.10\text{M})^m (0.30\text{M})^n}{k(0.10\text{M})^m (0.20\text{M})^n}$$

$$\frac{0.0225\text{ M/s}}{0.0150\text{ M/s}} = \left(\frac{0.30}{0.20}\right)^n = 1.5^n$$

$$1.50 = 1.5^n \quad [n=1]$$

For harder cases to find exponents, take log of both sides of the equation $\log(150) = \log(15^n) = n \log 15$

Step 2. Divide the rate law for the initial rate of one experiment by the rate law for the initial rate of a second experiment, such that the **concentration of the ONE REAGENT chosen from Step 1 changes**. This time however you may plug the order gleaned from Step 1 into your equation.

$$\frac{\text{Rate of experiment 3}}{\text{Rate of experiment 1}} = \frac{0.0600\text{ M/s}}{0.0150\text{ M/s}} = \frac{k[\text{NO}]_0^m [\text{H}_2]_0^n}{k[\text{NO}]_0^m [\text{H}_2]_0^n}$$

$$4.00 = \frac{k(0.20\text{M})^m (0.20\text{M})^n}{k(0.10\text{M})^m (0.20\text{M})^n}$$

$$4.00 = 2.0^m \quad [m=2]$$

What is the overall order for the reaction in question?

3rd order

Finally, for your purposes on an exam, it is sufficient to pick one experiment and plug in the initial rate, the initial concentrations and orders into the differential rate law equation to solve for your "k". (In practice, one would take an average of the k values from the experiments.)

Let's say we pick experiment 2 to solve for "k". Unlike the equilibrium constant "K", "k" should be written with units! The units are determined by verifying that the units are the same of both sides of the equation by dimensional analysis.

Rate of experiment 2

$$= k \cdot [NO]^m \cdot [H_2]^n$$

$$0.0228 \text{ M/s} = k \cdot (0.10 \text{ M})^2 \cdot (0.30 \text{ M})^1 \quad k = 7.5 \frac{1}{\text{M}^2 \cdot \text{s}} \text{ or } 7.5 \text{ M}^{-2} \cdot \text{s}^{-1}$$

Write the expression for the rate law, which should include the exponents and the k value (if the k value has been determined).

$$\boxed{\text{Rate of reaction} = \frac{-d[H_2]}{dt} = 7.5 \text{ M}^{-2} \text{ s}^{-1} \cdot [NO]^2 \cdot [H_2]^1}$$

Integrated Rate Law.

stop point
for midterm 2 //

Method 1 to Determine the Rate Law Expression: Using the **method of initial rates**, we saw that we could calculate the rate law expression (including orders of reaction, k value) from several different experiments where we'd keep one reagent concentration constant and altering the amounts of the others.

Method 2 to Determine the Rate Law Expression:

We can equally determine an expression for the rate law by looking at a single experiment, such that [Reactant] vs. time is measured at various time intervals, ideally with some reactant concentration data collected both before and significantly beyond the elapsing of the first **half life** ($t_{1/2}$). To do this, we will use the **Integrated Rate Law** expression. A = reagent

$t_{1/2} =$ Half-life ($t_{1/2}$) = first half life = time it takes to go from

$$[A]_0 \text{ to } \frac{[A]_0}{2}$$

What is meant by second half-life, third half-life, etc...?

Second half-life = time it takes to go from $\frac{[A]_0}{2}$ to $\frac{[A]_0}{4}$

third half-life = time it takes to go from $\frac{[A]_0}{4}$ to $\frac{[A]_0}{8}$

What is meant if I were to say "each successive (or consecutive) half-life is doubled"?

second half-life is two times longer than first half-life

third half-life is two times longer than second half-life

Deriving the Integrated Rate Law Expression

The differential rate law expression relates the rate of reaction to the concentration of reactants.

The Integrated Rate Law expression relates reactant concentration (at time a given time t) or $[A]_t$ vs. time.
 $[A]_t = \text{concentration (in M) of reactant A at time } t$.

Below we will derive a mathematical equation for the **Integrated Rate Law and for the half-life**, for the decomposition of a substance A (that is, looking at $A \rightarrow$ products) which will vary given the order of reactant. You are only responsible for the integrated rate law and half-life equations for the following orders of reaction: 0^{th} , 1^{st} and 2^{nd}

Let's start with what we know, the differential rate law expression and start deriving from there!

$$[A]^0 = 1$$

$$\begin{array}{c} 0^{\text{th}} \text{ order} \\ -d[A]/dt = k[A]^0 \end{array}$$

$$\begin{array}{c} 1^{\text{st}} \text{ order} \\ -d[A]/dt = k[A]^1 \end{array}$$

$$\begin{array}{c} 2^{\text{nd}} \text{ order} \\ -d[A]/dt = k[A]^2 \end{array}$$

Rearrange ks with dts
And d[A]s with [A]s

$$d[A] = -kdt$$

$$\frac{d[A]}{[A]} = -kdt$$

$$\frac{d[A]}{[A]^2} = -kdt$$

Do a definite integral** (see note) from time $t=0$ to time t on both sides of the equation.

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = \int_0^t -kdt$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = \int_0^t -kdt$$

Rearrange, keeping $[A]_t$

at left, k , t , $[A]_0$ at right in the equation. Put this in box below, Integrated Rate Law for zeroth order equation in a box. This is your **integrated rate law!**

$\ln[A]_t - \ln[A]_0 = -kt$
For first-order reaction, therefore are 2 forms of integrated Rate Law

$$\ln[A]_t = -kt + \ln[A]_0$$

$$\frac{1}{[A]_t} + \frac{1}{[A]_0} = -kt$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$y = mx + b$$

$$\text{First form in box: } \frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

Half-life equation for a second order reaction:

$$t_{\frac{1}{2}} = \frac{1}{[A]_0 k}$$

Setting $[A]_t = [A]_0/2$ and $t = t_{\frac{1}{2}}$, you can derive an expression for the **half-life**. This may be useful: put this in a box! for the half life of a zeroth order reaction:

$$t_{\frac{1}{2}} = \frac{[A]_0}{2k}$$

$$\ln x - ly = \ln \left(\frac{x}{y} \right)$$

$$\ln \left(\frac{[A]_0}{[A]_t} \right) = kt$$

$$\ln \left(\frac{[A]_0}{[A]_t} \right)^2 = kt \frac{1}{2}$$

$$\ln(2) = kt \frac{1}{2}$$

$$t_{\frac{1}{2}} = \frac{\ln 2}{K} \Rightarrow t_{\frac{1}{2}} = \frac{0.698}{K}$$

equation for the half-life equation for the first order reaction

(For this reaction:)

First half-life: time it takes to go from $1.24 \cdot 10^{-2} \text{ M}$ to $0.62 \cdot 10^{-2} \text{ M}$ $\approx 24 \text{ min}$ Second half-life: time it takes to go from $0.62 \cdot 10^{-2} \text{ M}$ to $0.31 \cdot 10^{-2} \text{ M}$ $\approx 24 \text{ min}$ First half-life = second half-life $\therefore 1^{\text{st}}$ order reaction

** For those of you that have NOT seen calculus and integrals, do not worry! You will NOT be asked to derive the integrated rate law or half-life expressions; you'll explore this in your math classes at one point! I derive the equation for the benefit of those that have; and essentially what one is doing here is applying this integral (tells you an area under a curve) to both sides of the equation (just like one gets an equality by taking the log of both sides of the equation).

** For those with no integral calculus background, you will instead MEMORIZE the equations in the boxes, with an understanding that there is a mathematical logic for their derivation.

Problem: For the following reaction: $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$, the following data was

collected. Determine the order of reaction. $\ln[\text{N}_2\text{O}_5]$ vs time is linear \therefore reaction is first order

$[\text{N}_2\text{O}_5]^{-1}$	Time (min)	$[\text{N}_2\text{O}_5]$ (mol/L)	$\ln [\text{N}_2\text{O}_5]$
81	0	1.24×10^{-2}	-4.39
108	10.	0.92×10^{-2}	-4.69
147	20.	0.68×10^{-2}	-4.99
200	30.	0.50×10^{-2}	-5.30
270	40.	0.37×10^{-2}	-5.60
257	50.	0.28×10^{-2}	-5.88
667	70.	0.15×10^{-2}	-6.50

$$\text{zeroth order: } t_{\frac{1}{2}} = \frac{[A]_0}{2k}$$

$$\text{first order: } t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$\text{second order: } t_{\frac{1}{2}} = \frac{1}{[A]_0 k}$$

There are 2 approaches one can use to determine the **order of reaction** with $[A]_t$ vs. time data.

Approach 1: First, knowing that zeroth, first and second order reactions are by far the most common, one can determine the **linearity of data plots**.

For zeroth order, the following plot will be linear: $[A]_t$ vs. time

For first order, the following plot will be linear: $\ln[A]_t$ vs. time

For second order, the following plot will be linear: $\frac{1}{[A]_t}$ vs. time

Approach 2: One can look at **successive half-lives**. How will the second-half-life for example relate to the first half-life if:

The reaction is 1st order?

Second half-life = First half-life
 \rightarrow since the half-life equation is independent of the starting concentration

0th order?

The second half-life is half as long as the first half-life for a zeroth order

2nd order?

The second half-life would be two times longer than the first half-life for a second order reaction

Integrated Rate Law: Reactions with More than One Reagent

One can always use **method of initial rates** to determine orders & rate constant for reactions with more than one reagent. However, one can determine the order for a reactant using an integrative rate law approach by using one reagent in **great excess** over the other. The rate constants obtained are called **pseudo rate constants** and the rate law obtained is called a **pseudo rate law** when one reagent is in great excess.



Let's consider the reaction of ethyl acetate with water: $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{C}_2\text{H}_5\text{OH}$

$$\text{Rate of reaction} = -\frac{d[\text{CH}_3\text{COOC}_2\text{H}_5]}{dt} = k[\text{CH}_3\text{COOC}_2\text{H}_5]^m[\text{H}_2\text{O}]^n \quad (\text{Equation 1})$$

Let's say one had water at 55 M (concentration of pure $\text{H}_2\text{O} = (1.00\text{g water}/0.001\text{ L water}) * (1\text{ mol}/18.02\text{ g}) = 55.5\text{ M}$) and reacted the water with only 0.010M ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$); water as we see is in significant excess. Due to the enormous excess, the concentration of water is essentially constant throughout the reaction, that is, $[\text{H}_2\text{O}]_0 = [\text{H}_2\text{O}]_t$. Whether the reaction is first, zeroth or second order with respect to water, the $[\text{H}_2\text{O}]^n$ will be constant over time.

We can therefore set $k[\text{H}_2\text{O}]^n = k'$, where k' is a pseudo rate constant; plugging equation ^{in this sentence} this into equation 1 we get:

$$\text{Rate of reaction} = -\frac{d[\text{CH}_3\text{COOC}_2\text{H}_5]}{dt} = k' [\text{CH}_3\text{COOC}_2\text{H}_5]^m$$

Under conditions with a great excess of water, measuring the $[\text{CH}_3\text{COOC}_2\text{H}_5]_t$ vs. time, you would observe that the reaction is first-order in $\text{CH}_3\text{COOC}_2\text{H}_5$. (How would we know this?) However, from method of initial rates experiment, the reaction of ethyl acetate with water happens to be first order in water, so the true overall order of reaction is =2; the reaction only appeared first order since a large excess of water was used.

*First order in $\text{CH}_3\text{COOC}_2\text{H}_5$ means that $m=1$
 \uparrow In $[\text{CH}_3\text{COOC}_2\text{H}_5]$ vs time gives a linear plot when a great excess of H_2O is present*

sum of n and m

A rate law that is first-order where one reagent is in great excess is called a **pseudo-first-order rate law** and a first order rate constant where one reagent is in great excess (such as k' in the example above) is called a **pseudo-first-order rate constant**.

Note: integrated rate law is nice since one can get orders of reaction from one experiment; however, sometimes one sees bizarre data with integrated rate law as the reverse reaction becomes important. If one sees bizarre data, one can always determine the orders and rate constant using the **Method of Initial Rates** seen earlier.

Problem: ^{14}C , as is true typically with decay of radioactive isotopes, degrades via a first order process with a half-life of 5730 years. A fossil sample is found that has 15 units of radiation. Let's say, based on recently-created ^{14}C samples of similar size, originally the fossil sample would have 100 units of radiation, calculate the age of the fossil (in years).

What is this technique called? Carbon dating

Now, you might get nervous setting up the mathematical equation for the first-order Integrated Rate Law: $\ln[\text{A}]_t = -kt + \ln[\text{A}]_0$.

First, you might think, how do I get k? (How would you get it?)

Half-life
equation for
first order reaction

$$t_{\frac{1}{2}} = \frac{0.693}{k} \quad 5730 \text{ years} = \frac{0.693}{k}$$

$$k = 1.21 \cdot 10^{-4} \text{ yr}^{-1}$$

In the equation $\ln([\text{A}]_0/\text{[A]}_t) = kt$, $[\text{A}]_t$ and $[\text{A}]_0$ are in units of molarity and here are units of radiation (or pressure or other concentration units in other problems). However, since the units cancel in the division $[\text{A}]_0/[\text{A}]_t$, you CAN plug in other initial units (such as initial units of radiation or initial units of pressure rather than initial molarity) in place of $[\text{A}]_0$ and other units at time t (such as units of radiation at time t or units of pressure at time t) in place of $[\text{A}]_t$. Consequently, we can calculate the age of the fossil without knowing the molarities.

So, plug in your units of radiation then solve.

$$\ln \left(\frac{\text{initial units of radiation}}{\text{units of radiation at time } t} \right) = kt$$

$$\ln \left(\frac{100 \text{ units}}{15 \text{ units}} \right) = 1.21 \cdot 10^{-4} \text{ yr}^{-1} t$$

$t = 1.6 \cdot 10^4 \text{ yr}$

Problem: A pseudo-first-order reaction is 40% complete at the end of 50. minutes. What is the value of the pseudo-first-order rate constant (in min^{-1})?

You might panic thinking that there are no concentrations here to work with for the (in this case pseudo) first-order rate law expression:

$$[\text{A}]_t = 0.60 [\text{A}]_0$$

at 50. min

$$\ln ([\text{A}]_0/[\text{A}]_t) = kt \quad \text{What can you do? (Then solve.)}$$

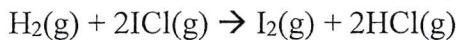
$$\ln \left(\frac{[\text{A}]_0}{0.60 [\text{A}]_0} \right) = k \cdot 50 \cdot \text{min}$$

$$K = 1.0 \cdot 10^{-2} \text{ min}^{-1}$$

Lecture Concepts 22. Theory Behind the Rate Law Expression, Reaction Mechanisms and Collision Model, including Activation Energy, Transition State and Catalysts

Define mechanism or reaction mechanism. \rightarrow step-by-step process by which a reaction occurs.

Consider the reaction below:



So far we've considered stoichiometry, equilibrium position and spontaneity for chemical reactions such as this, but we've yet to consider HOW exactly our reagents react with one another.

A proposed mechanism might be such that a reaction takes place in one single step (one step = one elementary step) or a series of elementary steps.

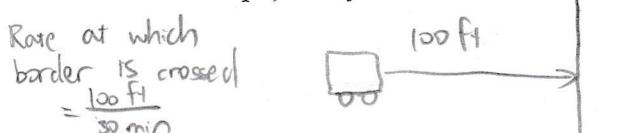
What sort of experimental data will narrow down our reaction mechanism proposals?

reaction rates

So how does kinetics help recognize whether a proposed mechanism is valid? As an example, let's say the kinetics data for the reaction above indicates that the reaction rate can be expressed as follows: $-d[\text{H}_2]/dt = k[\text{H}_2][\text{ICl}]$, that is the reaction is second order overall, and first-order in both hydrogen and iodine monochloride. \rightarrow rate law obtained experimentally

Now, one might imagine that elementary steps in a given reaction might take place slowly or quickly.

Let's think of steps for something completely different. Imagine you are 100 feet from the Canadian border driving, no cars in front of you, and you see a surly border agent who looks like he/she wants to give you a hard time. What step do you think will dictate the rate at which you cross the border, driving to the border or having the border agent process your papers? (The fast or the slow step?) Why?



Step 1: Driving to border = 10 seconds
Step 2: Getting past the surly border agent = 30 min

Similarly in a chemical reaction, you might imagine the rate of your reaction is dictated by the (circle \rightarrow slow or fast?) step of the reaction, which is called the rate - determining step, rate - limiting step or RDS step for short.

Step of a reaction = elementary

So, when one proposes a mechanism (the steps for a reaction), one should keep track that whatever elementary steps one proposes, the following 2 criteria must hold true:

criterion 1. The elementary steps must add up to the overall balanced equation for a reaction.

criterion 2. The orders of each reactant for the rate-determining step should be the same as the orders of each reactant determined from experiment (determined by, for example, Method of Initial Rates).

* Keep in mind that the orders of each reactant in an elementary step such as the rate-determining step, ARE the same as the coefficients for that step! Rate of step 1 = $K[H_2]^1 [ICl]^1$

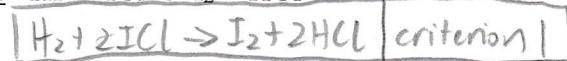
Is the below proposal for our reaction consistent with the kinetics data for the reaction $H_2(g) + 2ICl(g) \rightarrow I_2(g) + 2HCl(g)$? (Kinetics data showed reaction is first order in H_2 and first order in ICl .)

Criterion #2 is satisfied since the orders of the rate-determining (RD) step are the same as the orders seen from experiment

rate-determining step is slow step

Mechanism }
is valid
since two
criteria above
are satisfied.
Step 1 (slow): $H_2 + ICl \rightarrow HI + HCl$

+ Step 2 (fast): $HI + ICl \rightarrow I_2 + HCl$



Define reaction intermediate or intermediate

*Intermediate = substance that is produced first
and consumed after during the
course of a reaction*

What would be the reaction intermediate according to the proposed mechanism above?

HI

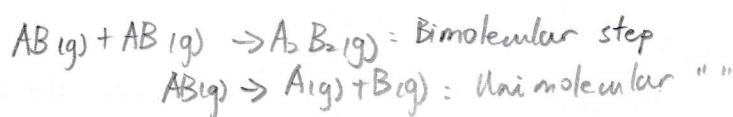
molecularity = the number of species that must collide (or break apart) to produce the reaction represented by an elementary step in a reaction mechanism. **Unimolecular** = when one molecule breaks apart in an elementary step. **Bimolecular** = when two species collide in an elementary step. **Termolecular** = when three species collide in an elementary step

} 3 types
of
molecularity

Why is a termolecular mechanism very rarely proposed for an elementary step of a chemical reaction? *unlikely for 3 substances to collide*

What is the molecularity of the rate-determining step for the reaction proposal above?

bimolecular // state the
molecularity
of the following
steps (if seen)



Mechanisms are theory and are never proven without a doubt; a mechanism can only be proposed and said to agree or be consistent with experimental data. Your goal in this course is to be able to look at a proposal and say that the proposal is consistent with experiment, not to generate your own proposals.

Caution: If an intermediate is present in a rate-determining step, one must consider the mathematical equation by which that intermediate is created when writing the rate law for the rate determining step.

Problem: Consider the reaction $2\text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO}_2\text{(g)}$. Experiments are done and the rate of reaction is observed to be $-\frac{d[\text{O}_2]}{dt} = k[\text{NO}]^2[\text{O}_2]$. Which, if any, of following mechanistic proposals consistent with the experimental data?

Two mechanism proposals

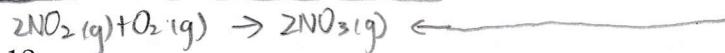
1st Proposal: Step 1. $\text{NO(g)} + \text{NO(g)} \rightarrow \text{N}_2\text{O}_2\text{(g)}$ (slow step with k_1 rate constant)

+ Step 2. $\text{N}_2\text{O}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO}_2\text{(g)}$ (fast step with k_2 rate constant)



2nd Proposal: Step 1. $\text{NO(g)} + \text{O}_2\text{(g)} \rightleftharpoons \text{NO}_3\text{(g)}$ (a fast equilibrium with K_3 equil. constant)

+ Step 2. $\text{NO}_3\text{(g)} + \text{NO(g)} \rightarrow 2\text{NO}_2\text{(g)}$ (slow step with k_4 rate constant)



Yes, no? Proposal 1?

$$\text{Rate of (RD) slow step} = k_1 [\text{NO}]^2 [\text{O}_2]^0$$

orders of RD step are not the same as orders seen from experiment

Criterion #2 is not satisfied; 1st proposal not valid.

Yes, no? Proposal 2?

$$\rightarrow \text{Rate of slow step} = k_4 [\text{NO}_3]^1 [\text{NO}]^1$$

Rate of slow (RD) step

$$= k_4 \cdot K_3 \cdot [\text{NO}] [\text{O}_2] [\text{NO}]$$

Rate of slow step

$$= k_4 \cdot K_3 \cdot [\text{NO}]^2 [\text{O}_2]^1$$

The intermediate was created in the first step by an equilibrium

$$K_3 = \frac{[\text{NO}_3]^1}{[\text{NO}]^1 [\text{O}_2]^1}$$

$$[\text{NO}_3] = K_3 [\text{NO}] [\text{O}_2]$$

plug this equation into rate law of RD steps

Collision Model and Activation Energy

Experimentally, reaction rates are seen to increase exponentially with temperature. If we think of reactions as (either a reactant breaking apart or) steps where two species colliding, it should make sense to you that enough the greater the average kinetic energy, the greater the likelihood of collision and collisions with the correct orientation of collision so as to promote a reaction.

T = Temperature (in K)

We saw that the $\ln K$ vs. $1/T$ has a negative slope for endothermic reactions according to the

van't Hoff equation: $\ln K = -\Delta H^\circ / RT + \Delta S^\circ / R$

$$\ln K = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$$

$$y = mx + b$$

Since a plot of $\ln k$ vs. $1/T$ is linear with a negative slope, Svante Arrhenius developed an analogous equation to show how k , the rate constant for a reaction, varies exponentially with temperature. Write one form of the Arrhenius equation below:

$$\ln k = \frac{-E_a}{R} \left(\frac{1}{T} \right) + \ln A$$

A = frequency constant
R = universal gas constant

where E_a is the activation energy (if in J/mol then: R? 8.314 J/K·mol T? Kelvin in units

Vant Hoff: $\ln K = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$

We'll write that Arrhenius equation again here: $\ln k = -E_a/RT + \ln A_{\text{eff}}$

So, what is the **activation energy**? Well, let's try to follow Arrhenius' line of thinking: if the equilibrium constant is regulated by the energy difference between the relative stability of reactants and products (ΔH°), he rationalized that the rate constant is regulated by a theoretical energy hill that reactants must travel over in order to be converted to products. This energy hill is known as the **activation energy**. E_a is always a positive number

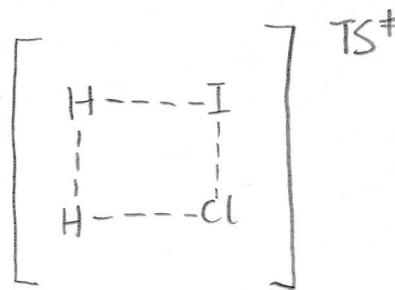
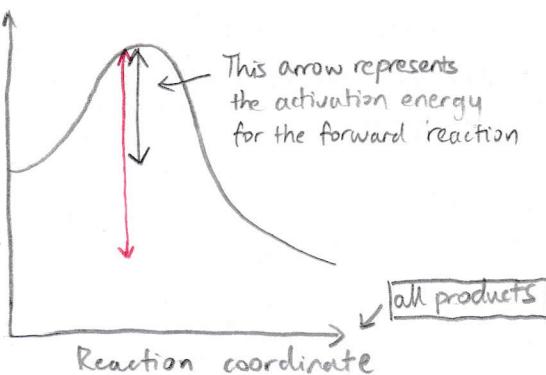
(Happens to be exothermic)

Let's consider the E_a as we plot potential energy vs. the reaction coordinate below for the rate-determining step of a few pages back: $H_2 + ICl \rightarrow HI + HCl$. What is a reaction coordinate?

reaction coordinate = measure of a reaction's progress

The red arrow shows the E_a for the reverse reaction

Energy
TS⁺ is between reactants and products
all reactants
Reaction coordinate
To show a TS⁺ we use a dashed line (---) to show bonds forming & bond breaking



1. Label the E_a for the forward reaction and E_a for the reverse reaction.
2. What does the $E_a(\text{forward reaction}) - E_a(\text{reverse reaction}) = \Delta E$ for a reaction (which is close to the all of a reaction)?
3. The top of the energy hill as reactants proceed to products is called the activated complex or the transition state or TS⁺, for short. Is this a stable arrangement of atoms? The TS⁺ is a high-energy, unstable atom arrangement
4. Draw how you think the top of the energy hill might appear.

Commonly, one shows a TS^+ in brackets with superscript TS^+ following end bracket.

What about the $\ln A$ where A is the so-called "**frequency constant**"? I think of A simply as a constant such that the $\ln A$ is the y-intercept in a plot of $\ln k$ vs. $1/T$. Sometimes A is said to be equal to $z^* p$, where z is related to collision frequency and p is a so-called **steric factor** (said to be related to proper orientation of collision for the reaction to proceed). My suggestion is not to sweat too much trying to understand A , but rather think of A as an experimentally-determined constant whose value simply is thought to take on every other aspect than E_a related to a successful collision, and a successful collision is needed for a reaction step to successfully occur.

or
bond-breaking or bond-breaking

One may also write the Arrhenius equation as follows:

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

A = Frequency constant

K = Rate constant

Show how this equation is the same as the Arrhenius equation on the previous page by taking the natural log of both sides. of equation

$$\ln K = \ln (A \cdot e^{-E_a/RT})$$

$$\ln e^x = x$$

$$\ln K = \ln A + \ln (e^{-E_a/RT})$$

$$\ln k = \ln A - \frac{E_a}{R} \cdot \left(\frac{1}{T} \right)$$

So, the Arrhenius equation again: $\ln k = -E_a/R(1/T) + \ln A$

An alternate useful form of the Arrhenius equations in problems is the following, think:

Since $\ln A$ is constant, $\ln k_1 + E_a/R(1/T_1) = \ln k_2 + E_a/R(1/T_2) = \ln A$

(where k_1 is the rate constant at a given temperature T_1 and k_2 is the rate constant at another temperature T_2), we can rearrange this equation to this very useful equation in problems:

$$\ln k_1 - \ln k_2 = \left[\ln \left(\frac{k_1}{k_2} \right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right] \leftarrow \text{another commonly used form of the Arrhenius equation}$$

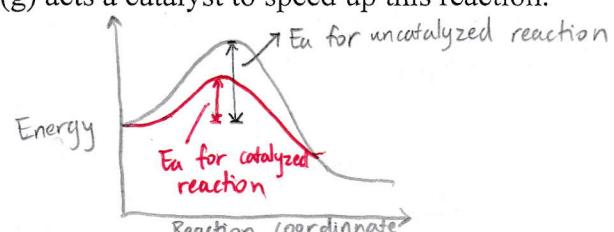
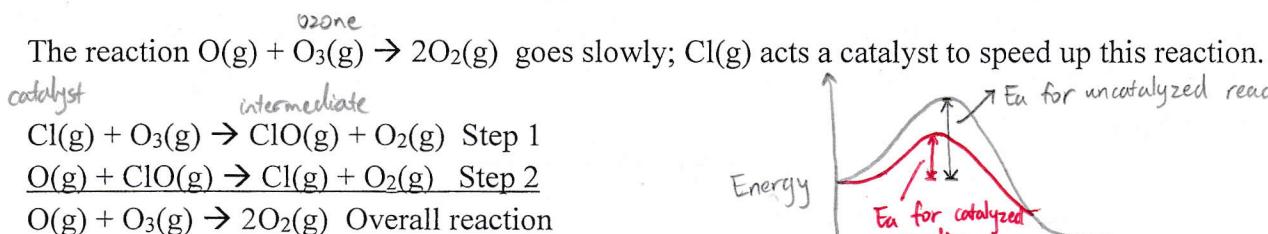
Problem: The rate constant of a first-order reaction is $3.46 \times 10^{-2} \text{ s}^{-1}$ at 298 K and 0.702 s^{-1} at 350. K. Calculate the activation energy (in kJ/mol). Solve.

$$\ln \left(\frac{3.46 \cdot 10^{-2} \text{ s}^{-1}}{0.702 \text{ s}^{-1}} \right) = \frac{E_a}{0.008314 \text{ J/K mol}} \left(\frac{1}{350 \text{ K}} - \frac{1}{298 \text{ K}} \right)$$

$$E_a = 50.2 \text{ kJ/mol}$$

Double check your answer: is a negative sign possible for the activation energy?

Catalyst= a substance added to a reaction to speed up the reaction **catalyze**= to speed up a reaction using a catalyst



Cl(g) produced from chlorofluorocarbons acts to catalyze the reaction of O_3 with O. A catalyst lowers the activation energy, but will not affect the ΔG (or K therefore) of the reaction (make a mini-graph at upper right). A catalyst is not present in the overall balanced equation for a reaction. A catalyst is a reactant in one elementary step and comes out as a product in a later elementary step. Since a catalyst is a product in a later step, it may be used over and over again.

Lecture Concepts 23. Introduction to Electrochemistry Terms

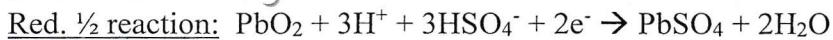
What is **electrochemistry**? Science that relates electrical energy and chemical energy

Oxidation involves a loss of e⁻s

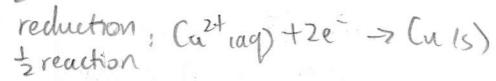
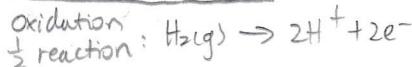
Reduction involves a gain of e⁻s

What common household example can you think of where you take advantage of electrochemistry? (see hints below)

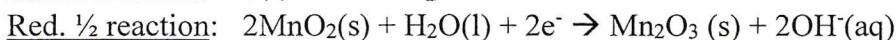
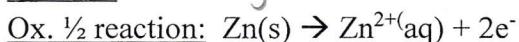
Lead-Acid battery



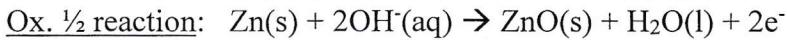
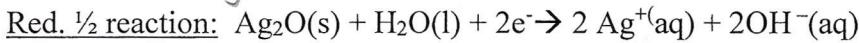
Reaction in beakers



Alkaline battery



Button battery



The above are all examples of what types of reactions? redox reaction

Electrolytic cell = setup that converts electrical energy into chemical energy.

Remind yourself: OIL RIG

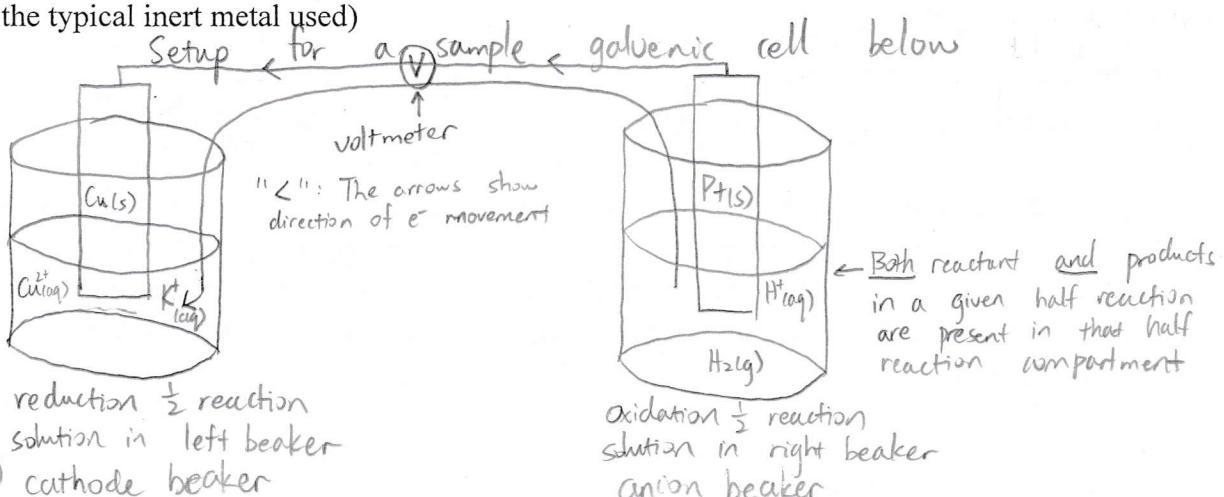
What is a **galvanic cell (galvanic cell= voltaic cell)?**

Galvanic cell = setup that converts chemical energy

Show by placing one half-reactions in one beaker and a second half-reaction in a second beaker, how one can think of a (crude) galvanic cell. Let's consider the following reaction:

$\text{H}_2(\text{g}) + \text{Cu}^{2+}(\text{aq}) \rightarrow 2\text{H}^+(\text{aq}) + \text{Cu}(\text{s})$. If there is a **neutral** metal present in a half-reaction, it is that metal that is dipped into the solution containing that half-reaction; if there is no neutral metal present in a half-reaction, an inert metal is dipped in the solution containing that half-reaction.

(Pt(s) is the typical inert metal used)



Metals dipped into each solution are called electrodes. These metals are connected often by alligator clips to a metal wire that allows electrons to flow.

The beaker (or metal in the beaker) where oxidation takes place is called the anode. The beaker (or metal in the beaker) where reduction takes place is called the cathode. Let's think of a mnemonic.

Show on the galvanic cell on the previous page in which direction the electrons will flow... think: will they flow from oxidation side to reduction side or in the reverse direction?

In the galvanic cell, electrons always flow from anode to cathode

One measures the electron flow with a device called a potentiometer or digital voltmeter, often shown on galvanic cell diagrams as a circled V. However, if one were to attach alligator clips from a wire to the two electrodes, current would flow for an instant and then cease. Why would the current cease? What's MISSING (state what this missing item might be made of)? The current ceases since there is not a complete circuit of charge flowing. What is missing is a salt bridge.

A salt bridge can be either ① a strip of absorbent paper soaked in a solution prior to placing the strip in 2 beakers of the galvanic cell or ② a glass "U"-shaped tube filled with a solution that has cotton plugs at both ends of "U" solution used contains an unreactive, commonly a neutral salt at 1.0 M or 0.10 M concentration

Once the salt bridge is set up a current results through the wire. Show the direction of the flow of ions (let's say K^+ or NO_3^-) from the salt bridge. *Let's imagine salt bridge used for galvanic cell on prior page has 1.0 M KNO_3 in it.*

So with the salt bridge set up, wires are clipped to electrodes and the digital voltmeter will give you a reading. This reading is known as the **cell potential**. The cell potential reading is in units of Volts.

Vocab: Volts = V = Joules/coulomb = J/C ; Cell potential = electromotive force = emf = $\xi_{cell} = \xi - E_{cell} = E_{cell}$
coulomb = C = fundamental SI unit of charge

In lab, you will polish the ends of the metal you will put into the solution (and possibly the ends attached to the alligator clips also) with steel wool. Why do you think this might be important?

One need to remove the oxide coating from the metal surface if one wants to be working with pure metal electrode.

Standard reduction potentials

To calculate the ξ°_{cell} from known reactions, one uses what are known as standard reduction potentials. Standard reduction potentials are found in tables in the appendix, written as $\xi^\circ_{red \frac{1}{2} rxn}$ or ξ° (in units of V) for the reduction.

E_{cell} = standard cell potential

$E_{red \frac{1}{2} rxn}$ = standard reduction potential

In tables of standard reduction potentials, you'll see reduction half-reactions, followed by a voltage (the $\xi^{\circ}_{\text{red } \frac{1}{2} \text{ rxn.}}$), such as:

<u>Half-reaction</u>	ξ°
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	2.87 V
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	1.99 V on the high end
$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.92 V
$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.05 V on the low end (and many more other half-reactions)

The degree symbol after the ξ° means the voltages were done at standard conditions which means that the aqueous solute reactants and products are at what concentration? Gaseous reactants and products at what pressure?

Aqueous solutes at 1M concentration, gases are at 1atm.

Naturally, a reduction half-reaction cannot occur without a simultaneous oxidation half-reaction. The ξ° value is the observed cell potential for the redox reaction with the reduction shown, such that the oxidation is the **standard hydrogen electrode**. The standard hydrogen electrode = the reaction $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$ in either the forward direction or the reverse direction, depending on whether the SHE is oxidized or reduced. (Standard hydrogen electrode =SHE) The $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$ was arbitrarily chosen as a standard and has an $\xi^{\circ}_{\text{red } \frac{1}{2} \text{ rxn}} = 0.00\text{V}$.

Under standard state conditions

An electrochemical galvanic cell will go spontaneously in the direction that $\xi^{\circ}_{\text{cell}}$ is positive. Consequently, the equation that will guide you when making a decision as to whether an oxidation-reduction reaction will occur successfully under standard state conditions is to consider the equation: $\xi^{\circ}_{\text{cell}} = \xi^{\circ}_{\text{red } \frac{1}{2} \text{ rxn.}} + \xi^{\circ}_{\text{ox. } \frac{1}{2} \text{ rxn.}}$. If the $\xi^{\circ}_{\text{cell}}$ value is a positive number, then the redox reaction will occur spontaneously under standard state conditions; if the $\xi^{\circ}_{\text{cell}}$ value is a negative number, then the reverse reaction will occur spontaneously under standard state conditions.

*$E_{\text{red } \frac{1}{2} \text{ rxn.}}$ value found in tables
(Appendix of Zumdahl)*

- Calculating the $\xi^{\circ}_{\text{cell}}$
1. If one reverses the half-reaction associated with a standard reduction potential ($\xi^{\circ}_{\text{red } \frac{1}{2} \text{ rxn.}}$), one gets the half-reaction associated with the standard oxidation potential (standard oxidation potential = $\xi^{\circ}_{\text{oxidation } \frac{1}{2} \text{ rxn.}} = \xi^{\circ}_{\text{ox. } \frac{1}{2} \text{ rxn.}}$). Whenever one reverses a reduction half-reaction to make it an oxidation half-reaction, one must simultaneously reverse the sign of the ξ° . So, for example, if the $\xi^{\circ}_{\text{red } \frac{1}{2} \text{ rxn.}}$ for $\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cd}(\text{s})$: -0.44, what is the value of the $\xi^{\circ}_{\text{oxidation } \frac{1}{2} \text{ rxn.}}$ for $\text{Cd}(\text{s}) \rightarrow \text{Cd}^{2+}(\text{aq}) + 2\text{e}^-$? $E_{\text{ox. } \frac{1}{2} \text{ rxn.}} = +0.44\text{ V}$
 2. If, to balance a redox equation, one needs to multiply all reactants and products of a half-reaction by an integer, what does one multiply ξ° for the half-reaction by?



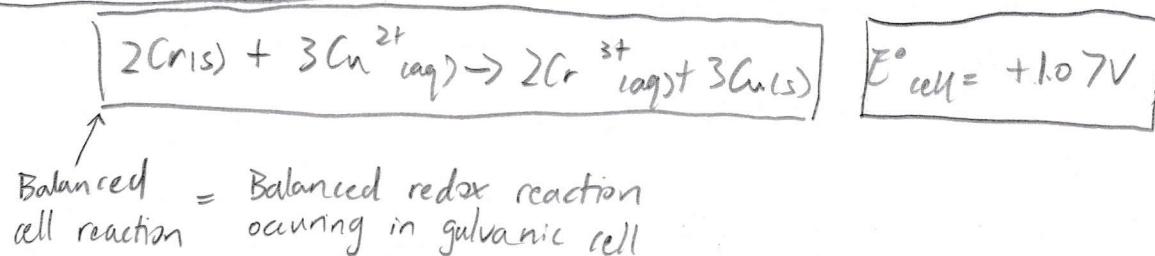
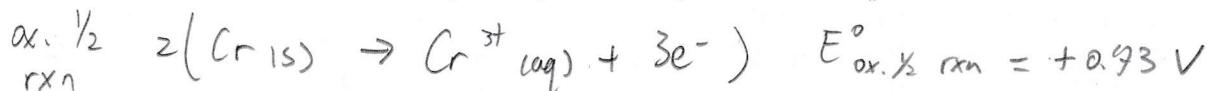
When multiplying half-reactions by an integer, why do the ξ° values not change? Remember: standard cell potentials (ξ°_{cell} values) are done under STANDARD STATE CONDITIONS, so the concentrations of all aqueous solute reactants and products are at 1M, and all gaseous reactants and products are at 1 atm regardless of the coefficient number sitting in front of each reagent. (standard cell potential = ξ°_{cell} value)

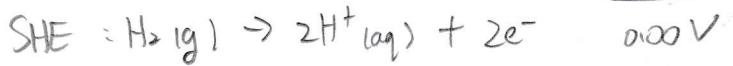
When you see a half-reaction like $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}$, keep in mind that under standard state conditions, if $\text{MnO}_4^-(\text{aq})$ is 1M, the $\text{H}^+(\text{aq})$ concentrations and $\text{Mn}^{2+}(\text{aq})$ will also be 1M in the galvanic cell set up under standard state conditions. The $\text{MnO}_4^- : \text{H}^+$ concentrations written in a 1:8 ratio simply shows that as the reaction is occurring, 8 moles of H^+ react per mole of MnO_4^- that reacts.

We see that the standard reduction potential (although must have specific concentrations or gas pressures as mentioned) does NOT depend on how many moles of each substance are present so is therefore considered an **intensive property**.

Problem: Calculate the ξ°_{cell} if one beaker contains Cu^{2+} (1M) and a Cu(s) electrode and a second beaker contains Cr^{3+} (aq) (1M) and Cr(s) electrode. Consider: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$ has an $\xi^\circ_{\text{red } \frac{1}{2} \text{ rxn}} = 0.34\text{V}$ and $\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Cr}(\text{s})$ has a $\xi^\circ_{\text{red } \frac{1}{2} \text{ rxn}} = -0.73\text{V}$.

Strategy: When considering what will be oxidized and what will be reduced, the reduction half-reaction that must be reversed to become an oxidation will be the reduction half-reaction that has the lowest value since this causes $\xi^\circ_{\text{cell}} = \xi^\circ_{\text{red } \frac{1}{2} \text{ rxn.}} + \xi^\circ_{\text{ox. } \frac{1}{2} \text{ rxn.}}$ to be a positive number.





Line Notation for Writing Electrochemical Cells

Let's consider two galvanic cells (electrodes attached by a wire, with a salt bridge). All ions shown are present at 1M concentration, all gases are at 1 atm pressure.

Galvanic cell #1: There is a Pt electrode, $\text{Cr}^{2+}(\text{aq})$ and $\text{Cr}^{3+}(\text{aq})$ present in one beaker and in second beaker there is $\text{Pb}^{2+}(\text{aq})$ and $\text{Pb}(\text{s})$ electrode.

Galvanic cell #2: $\text{Cu}^{2+}(\text{aq})$ and $\text{Cu}(\text{s})$ electrode are present in one beaker, the SHE (with Pt metal) is present in the second beaker.

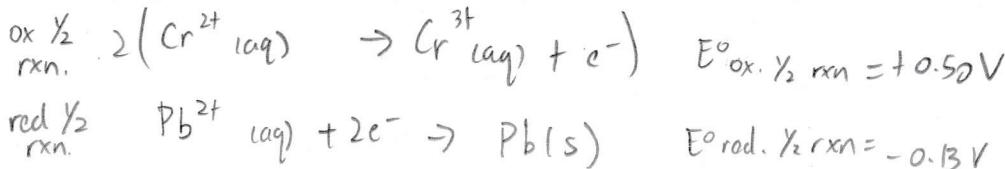
When one writes a galvanic cell using line notation, one considers the galvanic cell where the redox reactions occur spontaneously

1. Double vertical lines separate the anode compartment from the cathode compartment.
2. The anode is listed to the left of the double vertical line, while the cathode is listed to the right of the double vertical line. Think of a mnemonic device: electrochemistry is cool; what cools you in summer? all cold phases = state of matter
3. A single vertical line separates different phases in line notation (such as that between electrode and solution). Although, do note that some books show commas to separate gases from aqueous solutes.
4. Commas are always used to separate what? substance in the same phase in a department
5. The neutral metal electrodes in the cathode and anode compartments are written at far left and far right extremities in the line notation. Pressure/concentrations of reactants & products are optional in line notation.
6. One does not write coefficients of reactants or products in line notation.

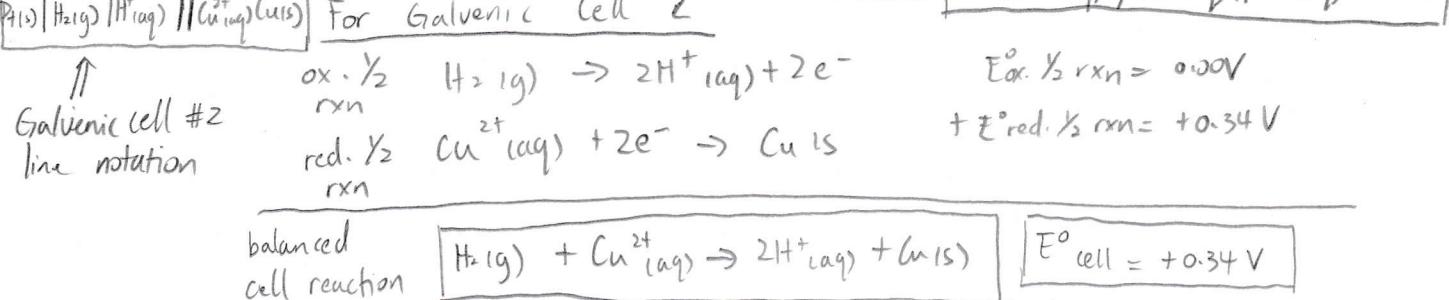
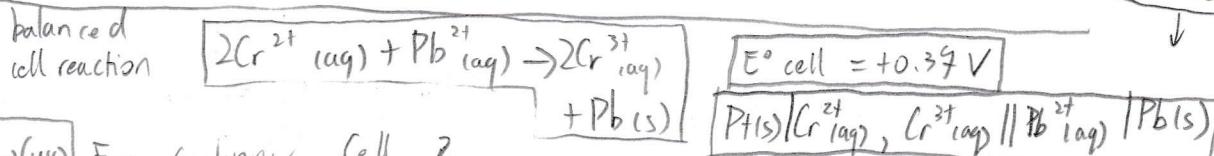
Line notation = Shorthand Way of Showing a Galvanic Cell

Problem: Write the above galvanic cells using line notation given the following standard reduction potentials: $\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$: -0.13V; $\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$: -0.50 V; $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$:

0.34V. For Galvanic Cell 1



Galvanic Cell #1
in Line Notation



$$\Delta E = q + w$$

Lecture Concepts 24. Electrochemistry Reaction Calculations. Spontaneity, Nernst Equation
(non-standard state cells), Concentration Cells, K_{sp}

Another way of approaching the concept of emf or ξ_{cell} , the voltage that you see passing through the galvanic cell is to remember that the cell is doing **work**, the work of moving those electrons through the distance of wire.

Since voltage is in units of Joules/coulomb, we can think of the voltage as work/charge

Or really $\xi_{cell} = w/q$ (where w is the work and in this case q is the charge (not the heat!)).

However, in an electrochemical system, the system is doing work on the surroundings just as in an expansion, so what will the sign of the work be? Negative

Now given that ξ_{cell} needs to be positive to be spontaneous, what sign should you put in front of w/q, a "plus" sign or a "minus" sign? (The value of q is a positive number.)

minus sign

We can substitute for this q, the expression $q = nF$, where n= coefficient of the electrons in the half-reactions when the numbers of electrons in both half-reactions have been equalized and F= 96 485 C/mol e⁻. F is called the Faraday constant and tells us the charge of what? mole of electrons

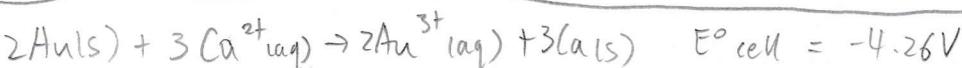
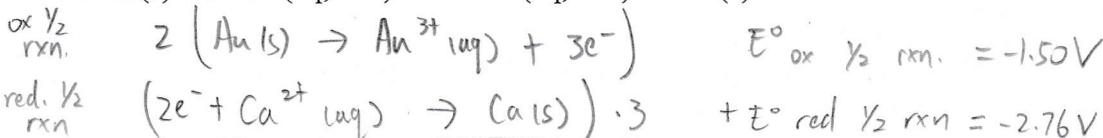
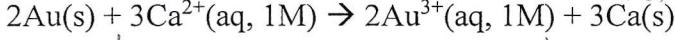
For w, we will write w_{max} instead, which stands for the maximum electrical work. Maximum work is used since some energy can be lost through frictional heating of the wire. In an earlier chapter, we learned that a change in a certain thermodynamic function was equal to the w_{max} (where w refers specifically to electrical work). Which one was it? $\Delta G = w_{max}$

Now, write the expression for calculating spontaneity that will be useful for problems (first, a generic expression, then one for standard state conditions).

$$E_{cell} = \frac{-w}{q} \quad E_{cell} = \frac{-\Delta G}{nF} \quad \boxed{\Delta G = -nFE_{cell}}$$

Problem: By calculating ΔG° from ξ_{cell}° , predict whether the reaction below would occur spontaneously in the forward direction as it is written (in a 1.0 L solution), given the following standard reduction potential data: $Ca^{2+} + 2e^- \rightarrow Ca: -2.76V$; $Au^{3+} + 3e^- \rightarrow Au: +1.50V$

Reaction as written has a negative E°_{cell} value, so is not spontaneous under standard conditions.



$$\Delta G^\circ = -nFE^\circ_{cell}$$

$$\Delta G^\circ = -(6\text{mol e}^-) \left(\frac{96485 \text{ C}}{\text{mol e}^-} \right) (-4.26V)$$

$$\boxed{\Delta G^\circ = 2.47 \times 10^6 \text{ J}}$$

Dependence of Cell Potential on Concentration; Looking at A Galvanic Cell with Non-Standard State Concentrations

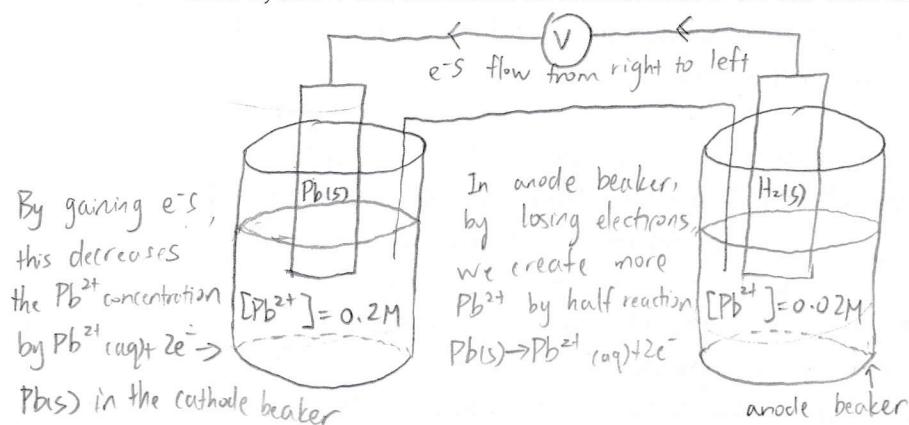
concentration cell = galvanic cell where identical electrodes are immersed in solutions of identical solutes, but such that the solutes are at different concentrations

If, let's say, we had $\text{Pb}^{2+}(\text{aq})$ and $\text{Pb}(\text{s})$ in two beakers connected by wire and salt bridge with both beakers with solutes at standard state conditions, what would the voltage be?

$$[\text{Pb}^{2+}] = 1\text{M} \text{ in both beakers and the } E^\circ_{\text{cell}} = 0.00\text{ V}$$

However, if we changed the concentrations of the lead ion in each of the beakers: one beaker now contains Pb^{2+} @ 0.2M and the second beaker contains Pb^{2+} @ 0.02M. In what direction will the electrons flow? Why (think about this from an entropic viewpoint)? (Draw the beakers below, show the direction of electron flow on the wire of the galvanic cell) Remember from entropy,

that it is more favoured in terms of probability to have a uniform distribution (an equal concentration that is) of particles in the 2 containers so, galvanic cell reacts to try to make concentrations same in 2 beakers



The Nernst Equation: Calculating the Voltage of a Non-Standard State Solution

Deriving the Nernst Equation

We learned that $\Delta G = \Delta G^\circ + RT(\ln Q)$ (equation 1) in the free energy chapter. We also recently learned that $\Delta G = -nF\xi_{\text{cell}}$ (equation 2) and $\Delta G^\circ = -nF\xi^\circ_{\text{cell}}$ (equation 3).

Substituting equation 2 and equation 3 into equation 1, we get:

$$-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + RT \ln Q_{\text{th}}$$

Divide both sides now by $-nF$ and you get the Nernst equation for any temperature. (Put this in a box.)

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q_{\text{th}}$$

↑ Eqn in box is the Nernst Equation

$$E_{\text{cell}} =$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q_{\text{th}} \leftarrow \text{Rewrote Nernst Equation}$$

However, since the temperature at which much electrochemical study is done is roughly 298K, the following expression for the Nernst equation is often observed. Plug in 8.314 J/K*mol for R, 298K for temperature, 96,485 C/mol e- for F and take advantage of the mathematical relationship $\ln Q = 2.3 \log Q$ to get an equation that you will put in a box below:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{(8.314 \text{ J/K}\cdot\text{mol})(298\text{K})}{n \cdot 96485 \text{ C/mol}} \cdot 2.3 \log Q_{\text{th}}$$

Nernst
equation
used for
reactions
at 298K

$$\boxed{E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591 \text{ J/C}}{n} \log Q_{\text{th}}}$$

If $Q = K$, that is if the redox reaction is at equilibrium, how much voltage (ξ_{cell}) do you think will be passing through our wire? How would you describe a battery where the redox reaction is at equilibrium?

↓ ↓
0.00V Battery's dead

Plugging in K for Q and the value of ξ_{cell} written above, make an equation (log K on the left side) by which one can quickly determine the equilibrium constant from the $\xi_{\text{cell}}^{\circ}$

$$0.00V = E_{\text{cell}}^{\circ} - \frac{0.0591 \text{ J/C}}{n} \log K_{\text{th}}$$

$$\log K_{\text{th}} = \frac{n E_{\text{cell}}^{\circ}}{0.0591 \text{ J/C}}$$

Remember that for the equations you've learned on the last two pages that "n" = coefficient of the electrons in the half-reactions when the numbers of electrons in both half-reactions have been equalized.

Problem: For the reaction $\text{Co}^{2+}(\text{aq}) + \text{Fe}(\text{s}) \rightarrow \text{Co}(\text{s}) + \text{Fe}^{2+}(\text{aq})$ calculate ξ_{cell} when $[\text{Co}^{2+}] = 0.15\text{M}$ and $[\text{Fe}^{2+}] = 0.68\text{M}$ and the K for this reaction @ 298 K (for problems, you should assume 298K if no temperature is given), given that the standard reduction potentials are: $\text{Co}^{2+} + 2e^- \rightarrow \text{Co}: -0.27\text{V}$ and that $\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}: -0.44\text{V}$ (Will K be large or small?)

Non-standard state concentrations; when you see this. Think, you need Nernst equation to find E_{cell} .

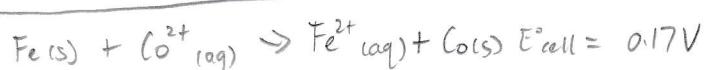
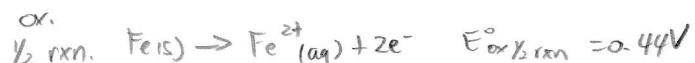
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591 \text{ J/C}}{n} \log Q_{\text{th}}$$

$$E_{\text{cell}} = 0.17\text{V} - \frac{0.0591}{2} \log \left(\frac{0.68}{0.15} \right)$$

$$\boxed{E_{\text{cell}} = 0.15\text{V}}$$

$$K_{\text{th}} = K_c \quad \log K_{\text{th}} = \frac{n E_{\text{cell}}^{\circ}}{0.0591\text{V}}$$

$$\log K_{\text{th}} =$$

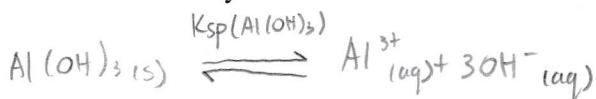


Chapter 16 Zumdahl

Lecture Concepts 25. Applying Equilibrium Constants to (Aqueous) Solution Chemistry 7.

Introduction to Solubility Equilibria and K_{sp} . ionic solid = ionic compound in solid form

In this section, dissolution of ionic solutes is investigated and how we express this in terms of equilibrium. Remember that an ionic solid, when dissolved in water, dissociates into the cations and anions that make it up. Write the reaction for the dissolution of a sample ionic solid (for example, Al(OH)_3) with equilibrium arrows. Think that equilibrium for an ionic solid dissolving is reached immediately.



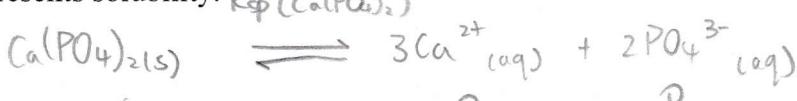
The dissolution of an ionic compound, like all reactions, has an equilibrium constant that describes its equilibrium state. This equilibrium constant is called the **solubility product constant**. (solubility product constant = solubility product = K_{sp}) Write this constant above the equilibrium arrows of the reaction shown above.

Do not confuse the terms **solubility** and **solubility product**. **Solubility**= the amount of a given substance that dissolves in a given volume of solvent at a given temperature. When solubility is expressed in terms of molarity (as it is most typically) it is called the **molar solubility**.

For book problems, where might one find K_{sp} values?

Problem: What is the molar solubility of $\text{Ca}_3(\text{PO}_4)_2$ if the $K_{sp}=1.3 \times 10^{-32}$ (Ignore any acid-base properties of the salt.)

Write out the reaction below for the dissolution of the ionic solid with equilibrium arrows (dissolution of ionic solid at equilibrium= solubility equilibria). The molar solubility of an ionic solid is equal to the “x” in the ICE Chart (set up in units of molarity) for an ionic solid dissolving. For example, think that for every “x” units of $\text{Ca}_3(\text{PO}_4)_2$ that dissolve, “3x” units of Ca^{2+} are created and “2x” units of PO_4^{3-} are created. Sometimes the letter “s” is written in place of “x” in an ICE Chart relating to solubility equilibrium to remind the student that the “s” represents solubility. $K_{sp}(\text{Ca}_3(\text{PO}_4)_2)$



(M)	I	C	E
	x		
	0	+3s	+2s

$$K_{sp} = [\text{Ca}^{2+}]_{eq}^3 [\text{PO}_4^{3-}]^2$$

$$1.3 \cdot 10^{-32} = (3s)^3 (2s)^2$$

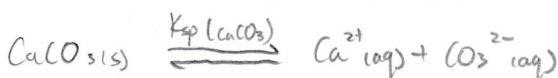
$$1.3 \cdot 10^{-32} = 108 s^5$$

$$s = 1.6 \cdot 10^{-7} M$$

Common Ion Effect.

Consider the solubility equilibrium for CaCO_3 dissolving (write out chemical reaction with equilibrium arrows below).

coefficient
is always
1 for reactions
with K_{sp} as
equilibrium
constant

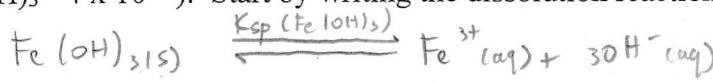


What will happen to the solubility of a slightly soluble ionic compound A if a soluble ionic compound that contains the anion of ionic compound A is added? For example, what will happen to the solubility of CaCO_3 if Na_2CO_3 is added? Whose principle tells you this?

Le Chatelier's Principle tells us that by adding Na_2CO_3 (which splits completely into Na^+ and CO_3^{2-}), the reaction above will shift to left to re-achieve equilibrium. The solubility of CaCO_3 decreases after this addition.

Common ion effect: Beware (~~of~~) hydroxides with small K_{sp} s!

Problem: Calculate the molar solubility of Fe(OH)_3 in a pH 7.00 buffer @ 25°C. ($K_{\text{sp}}(\text{Fe(OH)}_3) = 4 \times 10^{-38}$). Start by writing the dissolution reaction with equilibrium arrows.



What's wrong with the following? $(x)(3x)^3 = 4 \times 10^{-38}$

$$\text{pOH} = 7.00 \quad 10^{-\text{pOH}} [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

Now that we've thought about the above "what's wrong", let's solve.

$$K_{\text{sp}} = s(1.0 \times 10^{-7} + 3s)^3$$

$$4 \times 10^{-38} = s(1.0 \times 10^{-7})^3 \quad \leftarrow \text{small } K_{\text{sp}} \text{ approximation}$$

$$s = 4 \times 10^{-17} \text{ M}$$

Problem: Calculate the molar solubility of Cd(OH)_2 in a pH 7.00 buffer ($K_{\text{sp}} \text{ Cd(OH)}_2 = 5.9 \times 10^{-11}$). Set up the K_{sp} problem: $\text{Cd(OH)}_2(s) \rightleftharpoons \text{Cd}^{2+}(aq) + 2\text{OH}^-(aq)$, so $K_{\text{sp}} = [\text{Cd}^{2+}]_{\text{eq}}[\text{OH}^-]_{\text{eq}}^2$

Imagine you set up the ICE Chart as follows

$\text{Cd(OH)}_2(s) \rightleftharpoons \text{Cd}^{2+}(aq) + 2\text{OH}^-(aq)$			
(M)	I	0	1.0×10^{-7}
(M)	C	$+x$	$+2x$
(M)	E	$+x$	$1.0 \times 10^{-7} + 2x$

$K_{\text{sp}} = 5.9 \times 10^{-11} = (x)(1.0 \times 10^{-7} + 2x)^2$; if you assume $2x$ is negligible and set $5.9 \times 10^{-11} = (x)(1.0 \times 10^{-7})^2$, you would quickly see the fallacy of your assumption since $x = 5900$! In problems with relatively large K_{sp} values, the contribution of the hydroxide from the buffer becomes negligible. For metal hydroxide solubility problems, my recommendation is to try calculating the $[\text{OH}^-]_{\text{eq}}$ two ways: first where the " nx " is negligible and second where the $[\text{OH}^-]$ by taking $10^{-\text{pOH}}$ of the buffer is negligible. If the answer where " nx " indeed is negligible, use that answer, otherwise use the answer where the $10^{-\text{pOH}}$ of the buffer is negligible. (n = integer and " nx "= change in the ICE chart).

Troublesome to Students → Predicting the Effect of pH on Solubility of an Ionic Compound

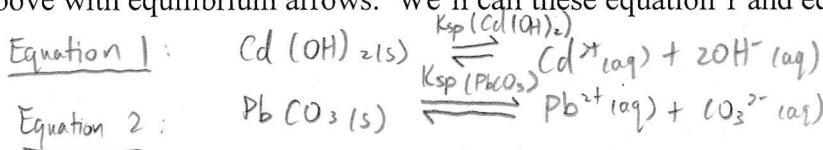
Problem: Predict which of the following will be more soluble in a pH 4.00 buffer than in a neutral solution.

- a) Cd(OH)₂
- b) PbCO₃
- c) PbCl₂

Focus on the anion to decide whether an ionic compound is more soluble at acidic pH than neutral pH

Scenario 1. If the anion of the ionic compound is **hydroxide** or the **conjugate BASE of a weak acid**, then the ionic compound will be more soluble at lower pH values. (The conjugate base of a weak acid is a weak base itself, so will react with H⁺(aq). To avoid confusion, we won't consider any conjugate bases of weak acids that have acidic properties).

Write the chemical reaction for the dissolving of ionic compounds a and b from the problem above with equilibrium arrows. We'll call these equation 1 and equation 2.



At pH 4.00, we have more H⁺(aq) than in the neutral solution. The H⁺(aq) will react with the OH⁻(aq) and the H⁺(aq) will react with the **conjugate base of a weak acid**.

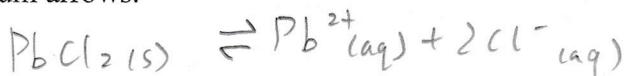


From Le Châtelier's Principle therefore, what is going to happen to the solubility as the hydroxide or CBWA is removed by reaction with H⁺(aq)?

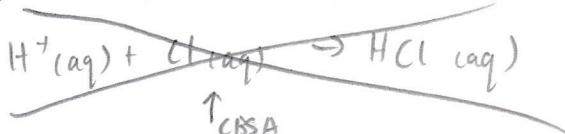
After removing CBWA or OH⁻ by reaction with H⁺ the reaction in equations 1 & 2 will shift to right to re-achieve equilibrium producing ions, making ionic compound more soluble

Scenario 2. If the anion of the ionic compound is the **conjugate base of a strong acid**, then the ionic compound is equally soluble under more acidic conditions as it will be under neutral conditions.

Write the chemical reaction for the dissolving of ionic compound c from the problem above with equilibrium arrows.



At pH 4.00, we have more H⁺ than in the neutral solution. What is this H⁺(aq) (strong acid) going to do with the CBSA?



The H⁺ does not react with the CBSA
(since the reverse reaction has a large K).

Enhancing your understanding. Calculating solubility in more acidic solution

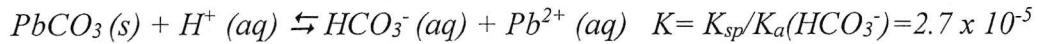
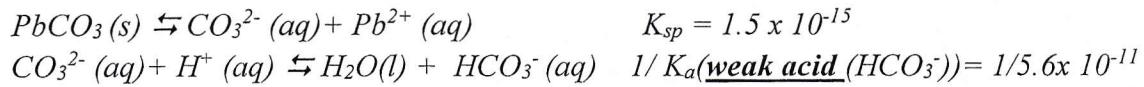
For your purposes, on an exam, all you need to do is be able to PREDICT whether an ionic compound (salt) is more soluble at lower pH than at neutral pH. NO CALCULATION REQUIRED.

However; for those of you more mathematically-minded, it can be helpful for getting these prediction problems right to know how solubility is calculated at a lower pH.

Let's say you were asked to calculate the solubility of lead carbonate at in a 0.10 M or a 1.0 M HCl solution.

Note the solubility were one to ignore the acid-base properties of the salt: $3.8 \times 10^{-8} M$.

Consider there are really two equilibria here; the solubility of lead carbonate and the reaction of carbonate (a CBWA) with H^+ . So, we ADD these two chemical equations together and therefore multiply their equilibrium constants get a new equilibrium expression.



We use the added chemical equation to calculate the solubility. The solubility as always is equal to the "x" in the ICE chart.

At 0.10 M HCl,

$$\frac{(+x)(+x)}{0.10 - x} = 2.7 \times 10^{-5} = K; \quad \text{solubility } x = 1.6 \times 10^{-3} M.$$

At 1.0 M HCl

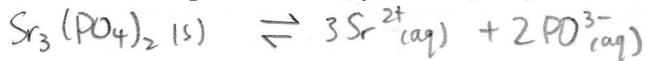
$$\frac{(+x)(+x)}{1.0 - x} = 2.7 \times 10^{-5} = K; \quad \text{solubility } x = 5.2 \times 10^{-3} M.$$

Q_{sp} is the reaction quotient for the reaction associated with the K_{sp} after all soluble compounds have dissociated into cation & anions.

Lecture Concepts 26. Applying Equilibrium Constants to (Aqueous) Solution Chemistry 8. The Equilibrium in Precipitation and Complex Ion Formation (large K examples!)

For the dissolving equation of an ionic solid $M_nX_i(s) \rightleftharpoons nM^{y+}(aq) + iX^{z-}(aq)$, the ion product $Q_{sp} = [M^{y+}]_0^n [X^{z-}]_0^i$ such that n, i, y and z are the appropriate integers for a given ionic solid, M= cation and X= anion of an ionic compound. $[M^{y+}]_0$ refers to the concentration of a given cation that would be present in a solution of interest after all soluble compounds present have dissociated, such as soluble salts splitting into the cations and anions that make up these soluble ionic compounds. $[X^{z-}]_0$ refers to the concentration of that anion present in a solution of interest after all soluble compounds present have dissociated, such as soluble salts splitting into the cations and anions that make up these ionic compounds. (vocabulary: Q_{sp} = ion product)

Write the chemical equation for $Sr_3(PO_4)_2$ dissolving with equilibrium arrows. Write a mathematical equation for Q_{sp} for $Sr_3(PO_4)_2$.



$$Q_{sp} = [Sr^{2+}]_0^3 [PO_4^{3-}]_0^2$$

If $Q_{sp} = K_{sp}$ for a given ionic solid, one has a **saturated solution**. A saturated solution means one has the maximum amount of given cations and anions dissolved that compose that given ionic solid.

If $Q_{sp} < K_{sp}$ for a given ionic solid, one has an **unsaturated solution**. No precipitate will form.

If $Q_{sp} > K_{sp}$ for a given ionic solid, one has a **supersaturated solution** and the given ionic solid will precipitate out!

Substance whose K_{sp} is given is possible precipitate

Reaction for K_{sp} of $Ce(IO_3)_3$

Problem: Will a precipitate form if 50. mL of 4.0×10^{-3} M $Ce(NO_3)_3$ is added to 300. mL of 2.0×10^{-2} M KIO_3 ? $K_{sp}(Ce(IO_3)_3) = 1.9 \times 10^{-10}$ (seeing values in molarity means all is dissolved)

(Remember: 4.0×10^{-3} M $Ce(NO_3)_3 \rightarrow 4.0 \times 10^{-3}$ M $Ce^{3+} + 1.2 \times 10^{-2}$ M NO_3^-) } Dissociate soluble ionic compounds into cations & anions first
 2.0×10^{-2} M $KIO_3 \rightarrow 2.0 \times 10^{-2}$ M K^+ + 2.0×10^{-2} M IO_3^-)

- a) Remember in precipitation reactions, a double displacement occurs, that is: cations exchange anion partners. What's our only possible precipitate?

cerium (II) nitrate + potassium iodide \rightarrow potassium nitrate + cerium (III) iodide

- b) Don't forget to dilute your ions (since you're mixing solutions) for this type of problem!

Calculate Q_{sp} and see how Q_{sp} compares to K_{sp} .

$$Q_{sp} = [Ce^{3+}]_0 [IO_3^-]^3$$

$$C_1V_1 = C_2V_2$$

$$Q_{sp} = (2.9 \times 10^{-3} M)(5.7 \times 10^{-3} M)^3$$

$$(4.0 \times 10^{-3} M Ce^{3+})(750. mL) = C_2 \cdot 1050. mL$$

$$Q_{sp} = 5.4 \times 10^{-10}$$

$$C_2 = 2.9 \times 10^{-3} Ce^{3+}$$

$$Q_{sp} > K_{sp}$$

$$C_1V_1 = C_2V_2$$

$$(2.0 \times 10^{-2} M IO_3^-)(300. mL) = C_2 \cdot 1050. mL$$

∴ a precipitate will form

$$C_2 = 5.7 \times 10^{-3} M IO_3^-$$

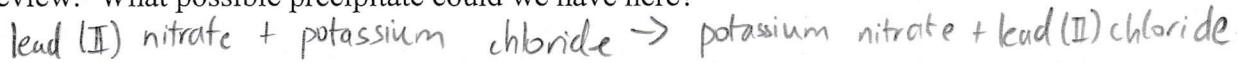
PbCl_2 is potential ppt.

since K_{sp} given for this compound.

Equilibrium Concentrations After a Precipitation

Problem: A solution is prepared by mixing 50.0 mL of 0.10 M $\text{Pb}(\text{NO}_3)_2$ with 50.0 mL of 1.0 M KCl. Calculate the concentrations of Pb^{2+} and Cl^- at equilibrium. ($K_{\text{sp}}(\text{PbCl}_2) = 1.6 \times 10^{-5}$)
 $(0.10 \text{ M } \text{Pb}(\text{NO}_3)_2 \rightarrow 0.10 \text{ M } \text{Pb}^{2+} + 0.20 \text{ M } \text{NO}_3^-; 1.0 \text{ M KCl} \rightarrow 1.0 \text{ M } \text{K}^+ + 1.0 \text{ M } \text{Cl}^-)$

Review: What possible precipitate could we have here?



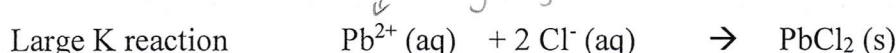
Review: How can we check if a precipitate actually forms? (Do the calculation)

$$Q_{\text{sp}} = [\text{Pb}^{2+}]_0 [\text{Cl}^-]^2_0 \quad \text{Don't forget to dilute Pb}^{2+}, \text{Cl}^-$$

$$Q_{\text{sp}} = (0.050 \text{ M})(0.50 \text{ M})^2 \quad \text{Obtained using } C_1V_1 = C_2V_2$$

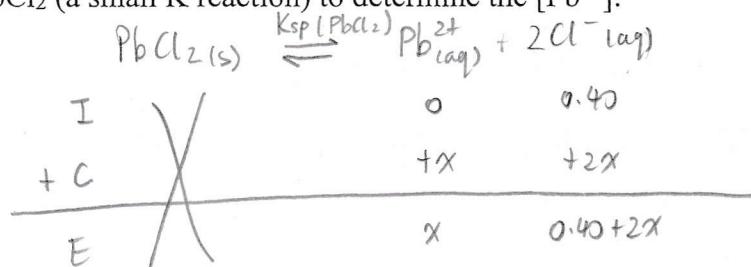
$$Q_{\text{sp}} = 0.0125 \quad Q_{\text{sp}} > K_{\text{sp}}, \text{PbCl}_2 \text{ precipitate forms}$$

If the dissolving of PbCl_2 or $\text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$ has a $K = 1.6 \times 10^{-5}$, then the reverse reaction $\text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightleftharpoons \text{PbCl}_2(s)$ has an equilibrium constant $K = 6.2 \times 10^4$. The reverse reaction $\text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightleftharpoons \text{PbCl}_2(s)$ is the net ionic equation for the precipitation of $\text{PbCl}_2(s)$ and like all precipitation reactions has a large K equilibrium constant. As always, one must do the reactions with large K values before proceeding to the small K reactions!



Before Large K reaction (M)	0.050	0.50
Change	-0.050	-0.10
After Large K reaction (M)	0	0.40

Now, hopefully you should realize that there's not 0 M Pb^{2+} present at equilibrium given that $K_{\text{sp}} \neq 0$, that the $\text{PbCl}_2(s)$ produced by the precipitation will dissolve to some extent, producing Pb^{2+} . So, now that the precipitation is complete, you can set up your ice chart for the dissolving of PbCl_2 (a small K reaction) to determine the $[\text{Pb}^{2+}]$.



$$K_{\text{sp}}(\text{PbCl}_2) = [\text{Pb}^{2+}]_{\text{eq}} [\text{Cl}^-]_{\text{eq}}^2$$

$$1.6 \times 10^{-5} = X(0.40 + 2X)^2$$

$$1.6 \times 10^{-5} = X(0.40)^2 \quad \leftarrow \text{small K approximation}$$

$$\boxed{X = [\text{Pb}^{2+}]_{\text{eq}} = 1.0 \times 10^{-4} \text{ M}}$$

$$\boxed{[\text{Cl}^-]_{\text{eq}} = 0.40 \text{ M}}$$

Fractional Precipitation = Selective precipitation = Technique by which one adds a compound that causes some ionic compounds to precipitate at a certain time, but not others.

Separating Ions by Fractional (Selective) Precipitation

Problem: AgNO_3 is added to a solution that contains both 0.010M Na_2CrO_4 and 0.010 M NaBr .

$K_{sp}(\text{Ag}_2\text{CrO}_4)$: 1.1×10^{-12} and $K_{sp}(\text{AgBr})$: 5.0×10^{-13} (assume no volume change on adding the silver nitrate)

(Remember: 0.010 M $\text{Na}_2\text{CrO}_4 \rightarrow 0.020 \text{ M Na}^+ + 0.010 \text{ M CrO}_4^{2-}$,

0.010 M $\text{NaBr} \rightarrow 0.010 \text{ M Na}^+ + 0.010 \text{ M Br}^-$) AgBr precipitates first, since it took less AgNO_3 (source of Ag^+ ions) to cause AgBr to precipitate

- a) What salt precipitates first? (Strategy: Find out at what concentration of Ag^+ added

$Q_{sp}=K_{sp}$ for each of the possible precipitable salts. Think that at all higher

concentrations of Ag^+ , the salt will precipitate out.) $\text{Ag}_2\text{CrO}_4(s) \rightleftharpoons 2\text{Ag}^{+}(aq) + \text{CrO}_4^{2-}(aq)$

$$K_{sp}(\text{AgBr}) = Q_{sp}(\text{AgBr}) = [\text{Ag}^+]_0 [\text{Br}^-]_0. Q_{sp}(\text{CrO}_4) = [\text{Ag}^+]_0 [\text{CrO}_4^{2-}]_0. \text{AgBr}(s) \rightleftharpoons \text{Ag}^{+}(aq) + \text{Br}^{-}(aq)$$

$$5.0 \times 10^{-13} = [\text{Ag}^+]_0 (0.010 \text{ M}) \quad 1.1 \times 10^{-12} = [\text{Ag}^+]_0^2 (0.010 \text{ M})$$

Above $\rightarrow [\text{Ag}^+]_0 = 5.0 \times 10^{-11} \text{ M}$

$$[\text{Ag}^+]_0 = 1.0 \times 10^{-5} \text{ M}$$

Above this concentration of Ag^+ , $Q_{sp} > K_{sp}$ for Ag_2CrO_4 and Ag_2CrO_4 will start to precipitate

- b) What is the concentration of Br^- (in M) when silver chromate starts to precipitate?

for AgBr and $\text{AgBr}(s)$ (Remember that most of the Br^- at this point has been removed by a large K reaction with Ag^+ to give AgBr precipitate, so the only Br^- present is that in equilibrium with the $\text{AgBr}(s)$ that was produced.)

$$K_{sp}(\text{AgBr}) = [\text{Ag}^+]_{eq} [\text{Br}^-]_{eq}$$

$$5.0 \times 10^{-13} = (1.0 \times 10^{-5} \text{ M}) [\text{Br}^-]_{eq}$$

$$[\text{Br}^-] = 5.0 \times 10^{-8} \text{ M}$$

- c) By adding silver nitrate, is this selective precipitation an effective method for separating Br^- ions from CrO_4^{2-} ions? (It's considered that if 99.9% (some books say 99%) of one ion is removed before the 2nd ion precipitates that the separation is effective.)

$[\text{Br}^-]$ was reduced from 0.010M to $5.0 \times 10^{-8} \text{ M}$ before Ag_2CrO_4 started to precipitate

$$\frac{5.0 \times 10^{-8} \text{ M } \text{Br}^-}{0.010 \text{ M } \text{Br}^-} \times 100 = 5.0 \times 10^{-4} \% \text{ Br}^-$$

is left when CrO_4^{2-} started to react with Ag^+

99.9995% of Cr^- was removed before CrO_4^{2-} reacts with Ag^+ in a precipitation reaction.

A Problem Combining Electrochemistry and Solubility Equilibria

Measuring K_{sp} of a sparingly soluble salt from ξ_{cell} data

Problem: Calculate the K_{sp} for the galvanic cell with the line notation shown, given that an $\xi_{cell} = 0.417\text{V}$ is observed. $\text{Ag}|\text{Ag}^+(\text{from a saturated Ag I sol'n}) \parallel \text{Ag}^+(0.100\text{M})|\text{Ag}$

anode || cathode

Note that this is a concentration cell. What species being oxidized? Reduced?

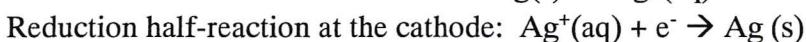
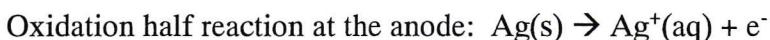
Ag(s) is oxidized (to $\text{Ag}^{+}\text{(aq)}$)

$\text{Ag}^{+}\text{(aq)}$ is reduced to Ag(s)

What is the ξ_{cell} for a concentration cell?

$$\xi_{cell}^\circ = 0.00\text{V} \quad (\text{when } [\text{Ag}^+] = 1.00\text{ M in both anode \& cathode compartments})$$

To set up your Nernst equation and solve for your unknown $[\text{Ag}^+]$ (in the saturated solution), think about the half-reactions for the concentration cell:



The $[\text{Ag}^+]$ is a product at the anode consequently and the $[\text{Ag}^+]$ is a reactant at the cathode. So, the $Q = [\text{Ag}^+]_{\text{at the anode}} / [\text{Ag}^+]_{\text{at the cathode}}$. A similar logic is applied to all concentration cells.

Assuming
298 K

for galvanic
cell

(unless told otherwise) $[\text{Ag}^+]_{\text{at anode}} = 8.8 \times 10^{-9}$

$$E_{cell} = E_{cell}^\circ - \frac{0.05915/c}{n} \log Q_{th}$$

$$0.417\text{ V} = 0.00\text{V} - \frac{0.05915/c}{1} \log \left(\frac{[\text{Ag}^+]_{\text{anode}}}{0.100\text{ M}} \right)$$



Once you know the $[\text{Ag}^+]$ in the saturated solution, the $[\text{Ag}^+]$ is equal to the $[\text{I}^-]$ in a saturated solution (remember, in a saturated solution $Q_{sp} = K_{sp}$) so the $[\text{Ag}^+][\text{I}^-] = K_{sp}$

$$(8.8 \times 10^{-9}) (8.8 \times 10^{-9}) = K_{sp}$$

$$K_{sp} = 7.7 \times 10^{-17}$$

THE
END