WorkSheet 4 **key**   Equilibrium

1. For the following equilibrium

$$CH_3COOH(aq) \leftrightarrow CH_3COO^-(aq) + H^+(aq)$$

if K = 1.8 x 10^{-5} at what [H$^+$] concentration will there be equal concentrations of CH_3COOH and CH_3COO^-?

[H+] = 1.8 x 10-5

2. For the following reaction

$$Fe_2O_3(s) \leftrightarrow 2Fe(s) + \frac{3}{2}O_2(g)$$
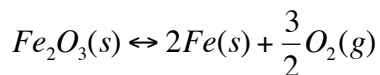
$\Delta_RH° = +825.5$ kJ mol^{-1}
$\Delta_RG° = +742.2$ kJ mol^{-1}

What is K for this reaction at 25°C?
T =298.15 K
R = 8.314 J K^{-1} mol $^{-1}$
$\Delta_RG° = +742200$ J/mol

At these conditions K = e^{-299}, which is effectively zero.

Given that air is 21% O_2, what is Q for this reaction in air?
Q = C_{O2} $^{3/2}$ Q = (0.21) $^{3/2}$ = 0.09623

Q is much larger than K at room temperature, and the reaction obviously heavily favors the formation of rust (K is practically zero).

Assuming that $\Delta_RH°$ and $\Delta_RS°$ are independent of temperature, approximate at what temperature Fe_2O_3 would first start to form any Fe in air.
Fe(s) would begin to form in air at temperatures above 2954 K.

3. True/False Decide if each statement is true or false and write out an explanation.

For the following reaction an increase in the total pressure will lead to an increase in the equilibrium constant

$$A(g) + 2B(g) \longleftrightarrow C(g)$$
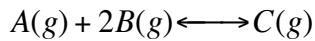
False, increasing the total pressure will not change the equilibrium constant, because K is determined by the partial pressures not the total pressures. Increasing the total pressure will cause the partial gas pressures to change (more C will be created, which leads to a decrease in A and B pressures), but the ratio of partial pressures will still equal to Kp.

For endothermic reactions, increasing the temperature will increase the equilibrium constant.
True. REMEMBER THAT K will vary with temperature (K is a function of T):
$\Delta G° = -RTlnK$

The van't Hoff equation gives the relationship between ΔH and the equilibrium constants for a reaction at two different temperatures.

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

If a reaction is exothermic (ΔH is negative "heat is a product"), K will decrease as T increases.
If a reaction is endothermic (ΔH is positive "heat is a reactant"), K will increase as T increases.

Adding reactants to an equilibrium mixture will lower the equilibrium constant

False, changing the concentration of chemical species, even when already at equilibrium, will not alter the equilibrium ratio of the concentrations (aka "K" of the reaction). Q, the reaction quotient, will change, but the reaction will shift in order to counteract the stress of addition of reactants. In this case, the addition of reactants A and B will cause the reaction to shift to the products, and form more C.

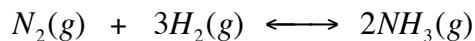The only way to alter the value of K is to vary the temperature.

For the following reaction, $K_p = K_c$

$$A(g) + B(g) \longleftrightarrow 2C(g)$$
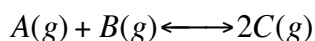
True. Kc will vary from Kp when Δn_{gas} (change in gas moles, products minus reactants) is non-zero. If $\Delta n_{gas} = 0$, Kc = Kp.
Remember, $Kp = Kc*(RT)^{\Delta n_{gas}}$, where R = 0.08206 Latm/molK

4. The following reaction is exothermic and has a $K_P = 1.9 \times 10^{-4}$ at 400°C

$$N_2(g) \; + \; 3H_2(g) \; \longleftrightarrow \; 2NH_3(g)$$

Which direction (if any) will the reaction have to shift toward to get back to equilibrium after the following changes (assume the change listed is the only change. i.e. increase in temperature at constant pressure) Explain your answer briefly.

Increase in the total pressure by compressing the volume
Shift to right (products)
If the total pressure is increased, the reaction will shift to the side with less moles of gas to counteract the applied stress.

Increase the temperature
Shift to left (toward reactants)
The reaction is exothermic, meaning "heat is a product." As the temperature is increased, more reactant will be produced, and the reaction will shift to the left.

Add 1 mol N_2, 3 mol H_2, and 2 mol NH_3
No change.
The reaction is N_2 (g) + $3H_2$ (g) ↔ $2NH_3$ (g); by adding a stoichometric amount of each species present in the equilibrium constant, the ratio of reactants to products is maintained, and the equilibrium is not disrupted.

Increase the total pressure by adding 2 moles of He gas at constant volume
The equilibrium constant should not change when inert gases are added at constant V since the partial pressures of each gas are unchanged.

* If 2 moles of He gas was added at constant pressure, it effectively dilutes the gases and is equivalent to lowering the partial gas pressures, which will shift the equilibrium to side with more moles of gas.

5. (note: this problem involves finding $\Delta_R H°$ and $\Delta_R S°$)
Calcium carbonate can decompose into calcium oxide and carbon dioxide by the following reaction.

$$CaCO_3(s) \longleftrightarrow CaO(s) + CO_2(g)$$

Given the data below
All data at 298K (you can assume H and S are independent of T)

Compound	$\Delta_f H°$ (kJ mol^{-1})	$\Delta_f G°$ (kJ mol^{-1})	S°(J K^{-1} mol^{-1})
CaCO$_3$ (s)	-1207	-1129	93
CaO (s)	-635	-604	40
CO$_2$ (g)	-393.5	-394.5	213.

What is K for this reaction at 298 K?
Remember how to calculate enthalpy, entropy and free energy changes for reactions using tabulated data:
 Very loosely stated, it is "sum of the products multiplied by their stoichiometric coefficients, minus the sum of the reactants multiplied by their stoichiometric coefficents".
For this particular reaction, the coefficients are all equal to one.
 ΔH°rxn = -635+-393.5 – (-1207) = 178.5 kJ mol^{-1}
ΔS°rxn = 213.5 + 40 – 93 = 160.5 J K^{-1} mol^{-1}
ΔG°rxn = -394.5 + -604 –(-1129) = 130.5 kJ mol^{-1}
K (298K)= exp[-ΔG°rxn/RT] = exp[-130500/(8.314*298)] = 1.33E-23

What would K be at 500 K?

Use the van't Hoff equation, which is found above and in your notes. Assuming deltaH is independent of T, we find

$$K_2 = \exp\left[\frac{-\Delta H_{rxn}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] * K_1$$

$$K_2(at\,500K) = \exp\left[\frac{-178500}{8.314}\left(\frac{1}{500} - \frac{1}{298}\right)\right] * 1.33 \times 10^{-23}$$

$$= 3.87 \times 10^{-22}$$

This should make sense qualitatively; since the reaction is endothermic, increasing the T should increase K.
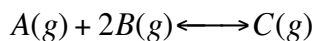
If 20 g of CaCO$_3$ were placed in an evacuated container, what would the partial pressure of CO$_2$ be in the container at equilibrium at 500 K if there is still some solid CaCO$_3$ remaining?
Write down the equilibrium expression for the reaction:
K = P$_{CO2}$
The pressure of the CO$_2$ (in atm) will be K(500 Kelvin).

6. (10 points)
For the reaction

$$A(g) + 2B(g) \longleftrightarrow C(g)$$

At some temperature you find P_A = 0.5 atm P_B = 0.25 atm P_c = 1.5 atm

What is K_P at this temp?
Kp = P_c/(P_a * P_b^2) = (1.5)/[0.5*0.25^2] = 48. Note that K is greater than one.

Is $\Delta_R G°$ positive negative or zero at this temperature? Explain.
Negative.
$\Delta_R G°$ = -RTlnK,
if K is greater than one, ln(K) is positive, which makes $\Delta_R G°$ negative, and the reaction spontaneous. Remember than reactions with large values of K actually occur, meaning they are spontaneous (thus requiring a negative $\Delta_R G$).
Do you think this reaction is exothermic or endothermic? Is there any way to tell?
There is no way to know for certain:
ΔG = ΔH - TΔS, and we know that the free energy change is negative.
If you were told that $\Delta rxnS$ was negative, the reaction would be exothermic (since T is always positive)
If you knew $\Delta rxnS$ was positive, the temperature would have to be known in order to find the sign of the enthalpy change.

If the total pressure was changed to 4 atm, would the number of moles of C increase, decrease, or stay the same?
Dalton's Law of partial pressures states that the total pressure of a gaseous system is equal to the sum of the partial pressures of the system's components.
From this, we know that the initial total pressure
P_{total}(initial) = (0.25+0.5+1.5) atm = 2.25 atm.

If the pressure was increased to 4 atm, the reaction would shift to the right, and more C would be formed.
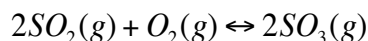
     Would K_p increase, decrease, or stay the same?
Stay the same – to change K, the temperature needs to be varied. Changing the total pressure has no effect on the value of the equilibrium constant K.

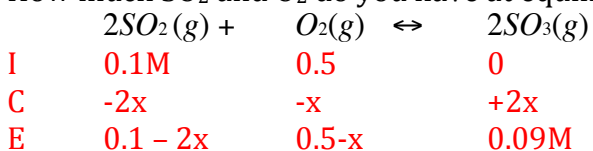You must get down your stoichiometry. Answer the following

7.
For this reaction

$$2SO_2(g) + O_2(g) \leftrightarrow 2SO_3(g)$$

You initially have concentration of SO_2 of 0.1 M, and O_2 of 0.5 M
At equilibrium you find you have a concentration of SO_3 of .09 M.

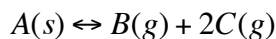How much SO_2 and O_2 do you have at equilibrium?

	$2SO_2(g)$ +	$O_2(g)$ $\leftrightarrow$	$2SO_3(g)$
I	0.1M	0.5	0
C	-2x	-x	+2x
E	0.1 – 2x	0.5-x	0.09M

Solve for X: 0.09 = 2x   x=0.045
$[SO_2]$ = 0.1 – 2*0.045 = 0.01 M
$[O_2]$ = 0.5 – 0.045 = 0.455 M

8. For this reaction

$$A(s) \leftrightarrow B(g) + 2C(g)$$

If you start out with only solid A, what is the ratio of the partial pressures of B to C at equilibrium?
$K = P_B * P_C^2$
Make a RICE diagram. Remember, A is a solid and has an activity of one.
At equilibrium, P_B = x and P_c = 2x, meaning P_B/ P_C = 0.5
If the partial pressure of B is found to be 0.01 atm at 298K, what is $\Delta_R G°$?
P_B = 0.01 atm, then P_c = 0.02 atm
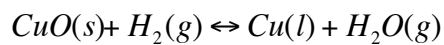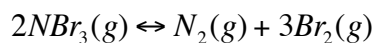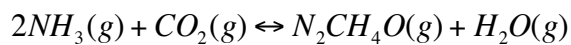Plugging into the equilibrium constant expression, K= (0.01)*(0.02)² = 4 E-6
$\Delta_R G°$ = -RTlnK
= - 8.314 J/(Kmol) * 298K * ln(4 E-6) = 30.7 kJ/mol
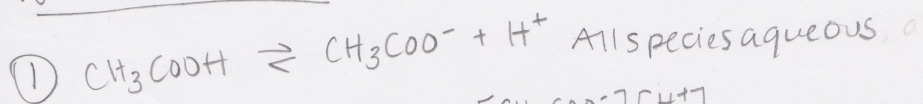

9. Practice Practice Practice

Write down the equilibrium constants for the following reactions
Make RICE diagrams for each assuming you start with either 1M concentrations of
gases or some amount of pure solid. Set up the algebra for how you would solve for
the equilibrium concentrations (you can't do the algebra since you don't have the
Ks)

$2NH_3(g) + CO_2(g) \leftrightarrow N_2CH_4O(g) + H_2O(g)$

$2NBr_3(g) \leftrightarrow N_2(g) + 3Br_2(g)$

$2KClO_3(s) \leftrightarrow 2KCl(s) + 3O_2(g)$

$CuO(s) + H_2(g) \leftrightarrow Cu(l) + H_2O(g)$

See handwritten notes. Please note that it would be very difficult to exactly solve for polynomials of the third order and greater (i.e. x^n $n \geq 3$) by hand—a fancy calculator or computer would be needed. We do, however, expect students to be able to solve for the zeroes of a quadratic equation (where the greatest value of n is 2) using a simple scientific calculator only.
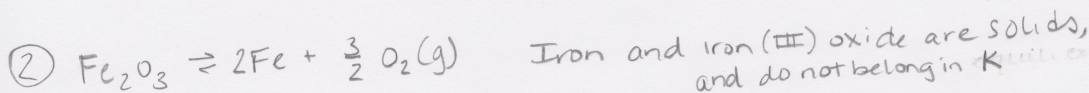
Worksheet 4 key

① $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ All species aqueous, a

$$K = 1.8 \times 10^{-5} = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$\nearrow$ (concentrations of CH_3COO^- and CH_3COOH)

If $\dfrac{[CH_3COO^-]}{[CH_3COOH]} = 1$, which means they are equal,

$$[H^+] = 1.8 \times 10^{-5} = K.$$

② $Fe_2O_3 \rightleftharpoons 2Fe + \frac{3}{2} O_2(g)$ Iron and iron (III) oxide are solids, and do not belong in $K_{equilibex}$

$$K_c = [O_2]^{3/2}$$

	O_2
I	0.21
C	$-\frac{3}{2}x$
E	$0.21 - \frac{3}{2}x$

$x \approx 0.14$

$$Q = C_{O_2}^{3/2} = (0.21)^{3/2} = 0.096$$

$Q \gg K$ (shift toward reactants)

$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ$$

$$\Delta S_r^\circ = \frac{\Delta G_r^\circ - \Delta H_r^\circ}{-T} = \frac{742.2 \text{ kJ/mol} - 825.5 \text{ kJ/mol}}{-298 \text{ K}}$$

$$\Delta S_r^\circ = 279.5 \text{ J/K}$$
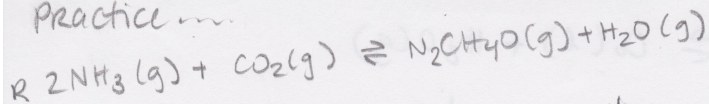
At what T would Fe_2O_3 form any Fe in air?

First, solve for ΔS_r° (above), and assume ΔH_r° and ΔS_r° are T-independent.

So, we need to answer the question, what T makes the reaction spontaneous ($\Delta G_{rxn} < 0$)?

$$\Delta G = \Delta H - T\Delta S = 0, \text{ so } T = \frac{\Delta H}{\Delta S} = \frac{825500 \text{ Jmol}^{-1}}{279.5 \text{ JK}^{-1}} = 2953 \text{ K}$$

PRACTICE...

R $2NH_3 (g) + CO_2(g) \rightleftharpoons N_2CH_4O (g) + H_2O (g)$

I	1	1	1	1
C	$-2x$	$-x$	$+x$	$+x$
E	$1-2x$	$1-x$	$1+x$	$1+x$

$$K = \frac{[N_2CH_4O][H_2O]}{[CO_2][NH_3]^2} = \frac{(1+x)^2}{(1-2x)(1-x)} = \frac{x^2+2x+1}{1-3x+2x^2}$$

$$K(1-3x+2x^2) - x^2 - 2x - 1 = 0$$

$$K - 3Kx + 2Kx^2 - x^2 - 2x - 1 = (2K-1)x^2 + (-3K-2)x + (K-1) = 0$$

use quadratic formula:

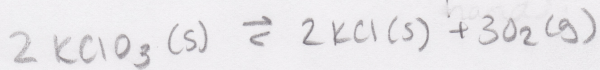$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{-(3K-2) \pm \sqrt{(-3K-2)^2 - 4(2K-1)(K-1)}}{2(2K-1)}$$

$2NBr_3 (g) \rightleftharpoons N_2 (g) + 3Br_2 (g)$
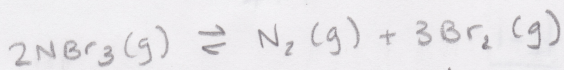
I	1	1	1
C	$1-2x$	$+x$	$+3x$
E	$1-2x$	$1+x$	$1+3x$

$$K = \frac{[N_2][Br_2]^3}{[NBr_3]^2}$$

$$K = \frac{(1+x)(1+3x)^3}{(1-2x)^2}$$

Do algebra, set the fourth order polynomial equation equal to zero, solve for zeroes (cannot do by hand)
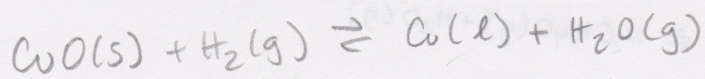
$2KClO_3 (s) \rightleftharpoons 2KCl(s) + 3O_2 (g)$

I	╳	╳	1
C			$-3x$
E			$1-3x$

$$K = [O_2]^3$$

$$K = (1-3x)^3 = (1-3x)(1-6x+9x^2) =$$
$$K = 1 - 6x + 9x^2 - 3x + 18x^2 - 27x^3 = -27x^3 + 27x^2 - 9x + 1$$
$$-27x^3 + 27x^2 - 9x + 1 - K = 0; \text{ solve for } x, \text{ plug into } [O_2] = 1-3x$$

$$CuO(s) + H_2(g) \rightleftharpoons Cu(l) + H_2O(g)$$

$$\begin{array}{ccc} 1 & 1 & 1 \\ -x & +x & +x \\ 1-x & 1+x & 1+x \end{array}$$

$$K = \frac{[H_2O]}{[H_2]} = \frac{1+x}{1-x} = K$$

$$K - Kx = 1 + x$$

$$K - 1 = x + Kx$$

$$K - 1 = x(1 + K)$$

$$[H_2O] = 1 + x$$

$$\frac{K-1}{1+K} = x$$

$$[H_2O] = 1 + \frac{K-1}{1+K}$$

$$\text{and} \quad [H_2] = 1 - \frac{K-1}{1+K}$$