Chem 105 Exam 4   Name ____Key_____

This exam is schedule for 75 minutes and I anticipate it to take the full time allotted. You are free to leave if you finish. In multiple part problems, points awarded will not be penalized for incorrect answer on previous parts, so simply **move on if you get stuck on one part**. If you need to, make up an answer for the previous part. Always neatly show work for partial credit.

1. Using the graphs below and this: $y = -0.163x + 2.525$
   a. Determine the rate law

$$\text{rate} = k\,[H_2O_2] = 0.163\ s^{-1}\,[H_2O_2]$$

   b. Determine the rate constant – make sure to include the correct units.

$$0.163\ s^{-1}$$

   c. Determine the initial concentration of H_2O_2.

$$\ln[H_2O_2]_0 = 2.525 \qquad [H_2O_2]_0 = 12.5\ mM$$

   d. Determine the initial rate of the reaction.

$$\text{rate} = 0.163\ s^{-1}(12.5\ mM) = 2.036\ \frac{mM}{s}$$
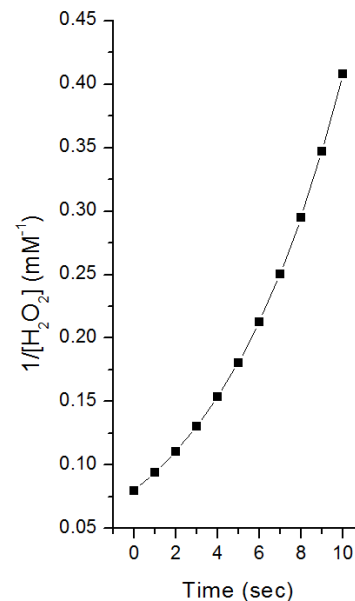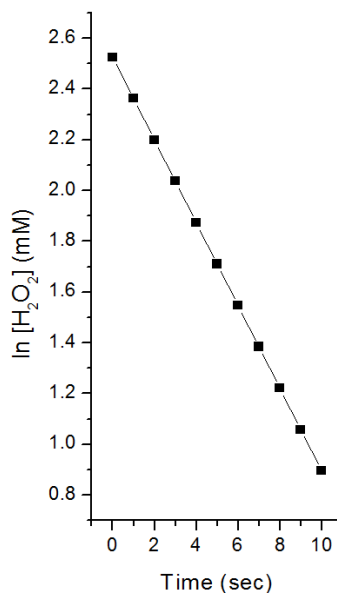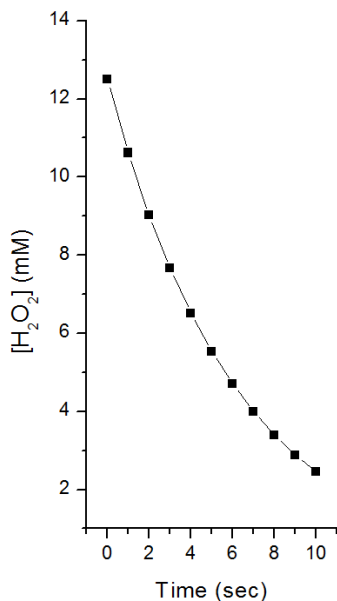
2. What are three ways to change the rate of a reaction? Clearly explain each of your answers.

① add a catalyst. this will decrease the E_a and therefore k

② change the concentration of reactants $\text{rate} = k[A]$ ←if $[A]$ changes, so does the rate

③ change Temp. this will change the rate constant (k)

3. Define the first and second laws of thermodynamics and explain what impact they have on the important concepts of thermodynamics that we have discussed in class.

1st law = Energy must be conserved. From this idea, we were able to describe how the internal energy of a system can change heat is exchanged with the surroundings or work is done on or by the system. From the 1st law, the state function of enthalpy was introduced.

2nd Law = the universe must tend toward disorder. This is where the term of entropy is introduced and how we learn about reaction spontaneity. Consequently, ΔG comes from the 2nd law.

4. Combustion engines are not 100% efficient; that is, not all of the energy produced from the combustion reaction results in work (you know, to make your car move). What happens to the rest of the energy?

It escapes as heat.

5. In your own words, describe why and which direction a reaction "shifts" when Q > K.

There are too many products, so the components of the reaction must adjust so that equilibrium ratio is established (reactants will form) and it becomes energetically favorable for the reverse reaction to happen ($\Delta G > 0$)

6. Why are equilibrium constants sensitive to temperature? In other words, why does K change with T?

Because heat can be treated as a reactant or product. By changing the temperature of a reaction, this influences the "concentration" of heat. According to LeChattlier's Principle, the reaction must adjust to reestablish the proper ratio of reactants and products; this necessarily changes the ratio and therefore K.

What can make an equilibrium constant temperature independent? $\Delta H = 0$

7. H_2O has a higher enthalpy of vaporization than C_2H_6. Why? Stronger intermolecular forces (H bond vs. LDF only)

8. Consider the two reaction coordinates below. Answer each of the following questions. **If it is not possible to determine, say that.**

1

2
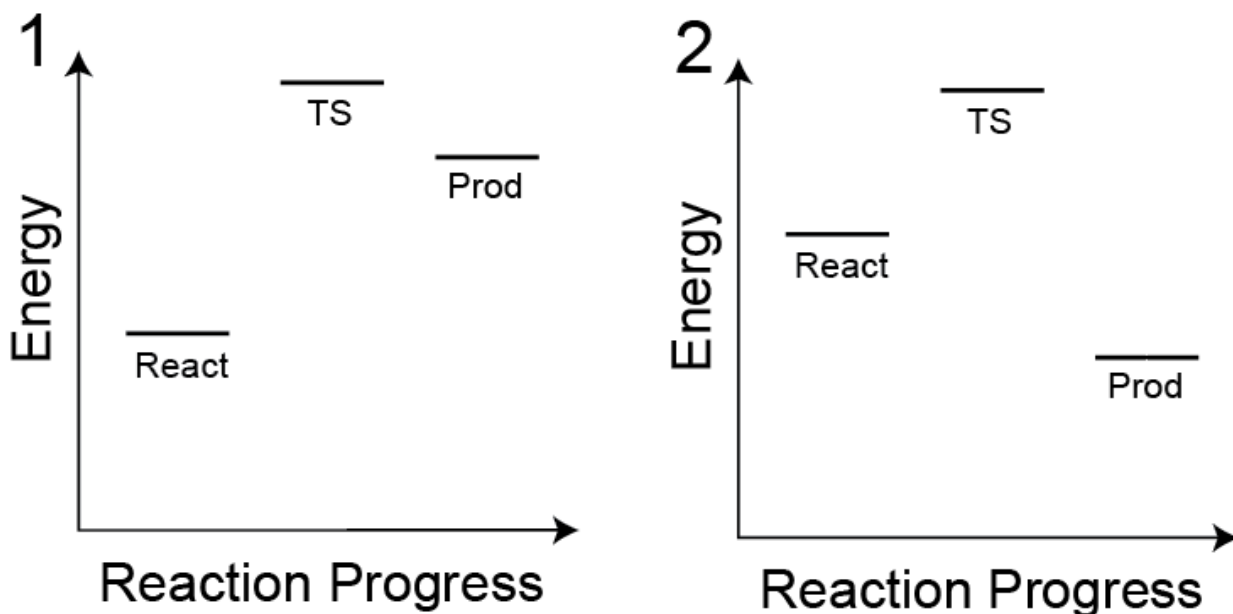
a. Which reaction has a larger equilibrium constant? 2 the 1st reaction is non-spontaneous and the 2nd is spontaneous

b. Which reaction has a larger rate constant? 1 – the 1st reaction has a smaller activation energy

c. Which reaction is spontaneous?   2 (products < reactants)

d. Which reaction has a rate constant for the forward reaction greater than the reverse reaction (i.e. $k_{for} > k_{rev}$) 2 – the activation energy for the reverse reaction (prod → react) is smaller than for the forward

e. Which reaction is exothermic? No way to tell. We can only see that the reaction is spontaneous or non-spontaneous but not why.

f. Which reaction might have $\Delta H > 0$ and $\Delta S < 0$? the 1st one. It is non-spontaneous and each of these are unfavorable.

9. Consider the following reaction. Circle the most correct choice for ΔH, ΔS, and ΔG. Clearly explain your choice for each.

$$S \ (s) + 3 \ Cl_2 \ (g) \rightleftharpoons SCl_6 \ (s)$$

breaking 3 bonds but making 6

| $\Delta H > 0$ | $\Delta H < 0$ | not able to determine |

Cl–Cl
Cl–Cl
Cl–Sl

Cl–S–Cl structure

| $\Delta S > 0$ | $\Delta S < 0$ | not able to determine |

| $\Delta G > 0$ | $\Delta G < 0$ | spontaneous at high temperatures | spontaneous at low temperatures |

↓ # of molecules AND # of gas molecules

@ low T, TΔS is small

10. Consider the following reaction:

$$CS_2 \text{ (g)} + CO_2 \text{ (g)} \rightleftharpoons 2\, CO \text{ (g)} + 2\, S \text{ (s)}$$
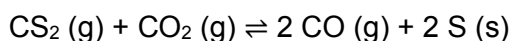
a. Using the information available at the back of the exam, calculate $\Delta G°$ and $\Delta H°$.

$\Delta G° = 2(-137.2) - [67.1 + -394.4] = 52.9 \text{ kJ/mol}$

$\Delta H° = 2(-110.5) - [116.7 + -393.5] = 55.8 \text{ kJ/mol}$

b. What is the equilibrium constant at 25 °C?

$\Delta G° = -RT \ln K$

$52,900 = -8.314(298.15) \ln K$

$\ln K = -21.34$

$K = 5.4 \times 10^{-10}$

c. Calculate $\Delta S°$

$\Delta G° = \Delta H° - T\Delta S°$

$52,900 = 55800 - 298.15 \, \Delta S°$

$\Delta S° = 9.73 \dfrac{J}{mol \cdot K}$

d. If 1 M of all reactants and products are combined at 25 °C, will this reaction shift to products or reactants? Please explain your answer.

Reactants $\Delta G° > 0$ These are standard conditions!

$\searrow$ reactants

e. 2 atm of CS_2 and 2 atm of CO_2 are combined at 1000 K. When equilibrium is reached, the pressure of CO is 0.1214 atm. Determine the equilibrium constant at this temperature.

$$CS_2 + CO_2 \rightleftharpoons 2\,CO + 2S(s)$$

	2	2	O	X
I	2	2	O	X
C	-X	-X	+2X	
E	2-X	2-X	2X	

$K = \dfrac{(0.1214)^2}{(2-0.0607)^2}$

$K = 3.92 \times 10^{-3}$

$P_{CO} = 2X = 0.1214$

$X = 0.0607$

f. Calculate ΔG if 0.04 atm of CO, 2 atm of CO_2, and 1 atm of CS_2 are added to a reaction flask at 1000 K. If you didn't calculate an equilibrium constant in part e, use 1.25×10^{-3}.

$\Delta G° = -8.314(298.15) \ln 3.92 \times 10^{-3} = 13,736.8 \dfrac{J}{mol}$

$\Delta G = 13736.8 + 8.314(1000) \ln \dfrac{(0.04)^2}{(2)(1)} = -59,286 \dfrac{J}{mol}$

11. **Complete one of the problems on this page**. You can answer more for extra credit. Please use the next page to show your work if you need more space.

a. Determine the total pressure at equilibrium if 4 grams of carbon and 1 atm of H_2 are added to a reaction flask at 500 °C.

$$C(s) + 2 H2 (g) \rightleftharpoons CH_4 (g) \qquad Kp = 2690 \text{ atm}^{-1} \text{ at } 500 °C$$
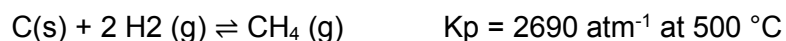
b. Using the information in the table below, determine the heat capacity of solid CS_2 if 2.34 kJ of heat is released when 10 grams of liquid CS_2 is cooled from 46.3 °C to -150 °C.

c. Determine the standard molar entropy of fusion and vaporization for CS_2.

Thermodynamic values for CS$_2$

T_b (°C)	T_m (°C)	ΔH_{fusion} (kJ/mol)	$\Delta H_{vaporization}$ (kJ/mol)	C (solid) J / (mol K)	C (liquid) J / (mol K)	C (gas) J / (mol K)
46.3	-110.8	4.39	27.65		78.99	46.55

d. Use the method of initial rates to determine the rate law and rate constant.

Experiment	[NO$_2$] (M)	[CO] (M)	Rate (M s^{-1})
1	0.15	0.15	0.001974
2	0.30	0.15	0.007898
3	0.60	0.30	0.25272
4	0.60	0.60	2.02176

e. Using the information at the back of the exam, determine the temperature that is needed to make this reaction spontaneous.

$$CS_2 (g) + CO_2 (g) \rightleftharpoons 2 CO (g) + 2 S (s)$$

a) $C_{(s)} + 2H_{2(g)} \rightleftharpoons CH_{4(g)}$
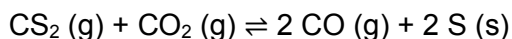
I	1 atm	0
C	$-2x$	$+x$
E	$1-2x$	x

$2690 = \dfrac{x}{(1-2x)(1-2x)} = \dfrac{x}{1-4x+4x^2}$

$2690 - 10760x + 10760x^2 = x$

$0 = 10760x^2 - 10759x + 2690$

$x = 0.504$ or 0.495
$\quad\quad\times$
not possible

$P_{H_2} = 1 - 2(0.495) = 0.01$ atm

$P_{CH_4} = 0.495$

$\boxed{P_{Tot} = 0.495 + 0.01 = 0.505 \text{ atm}}$

b. $\Delta H_{Tot} = \dfrac{-2340 \text{ J}}{0.1313} = -17819.1 \dfrac{\text{J}}{\text{mol}}$

$10 g \; CS_2 \left| \dfrac{\text{mol}}{76.15 g} = 0.1313 \text{ mol} \right.$
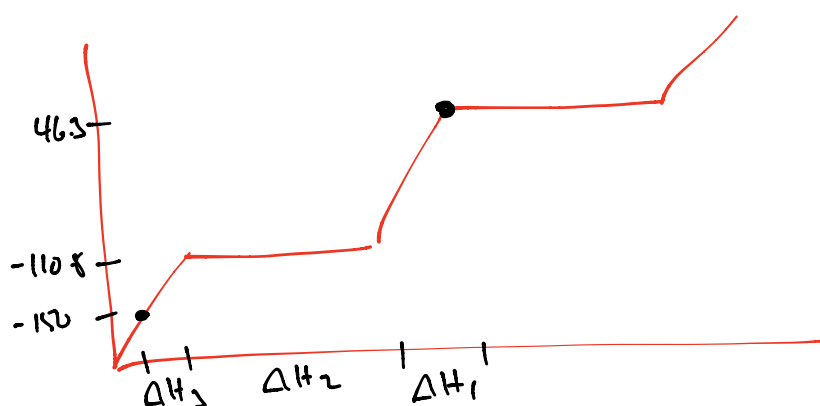
$\dfrac{-17819.1 \text{ J}}{\text{mol}} = -12409.3 + ^-4390 + \Delta H_3$

$\Delta H_1 = 78.99 \dfrac{\text{J}}{\text{mol} \cdot K} (-110.8 - 46.3) = -12409.3 \dfrac{\text{J}}{\text{mol}}$

$\Delta H_3 = -1019.8 \dfrac{\text{J}}{\text{mol}} = C(-150 - ^-110.8)$

$\Delta H_2 = -4390 \dfrac{\text{J}}{\text{mol}}$

$\boxed{C = 26.02 \dfrac{\text{J}}{\text{mol} \cdot K}}$

c. @ T_m $\Delta G = 0$ for $S \rightleftharpoons l$ $\Delta H^\circ_{fus} - T_m \Delta S^\circ_{fus} = 0$

$$\Delta S^\circ_{fus} = \frac{\Delta H^\circ_{fus}}{T_m} = \frac{4390 \frac{J}{mol}}{-110.8 + 273.15} = 27.04 \frac{J}{mol \cdot K}$$

$$\Delta S^\circ_{vap} = \frac{\Delta H^\circ_{vap}}{T_b} = \frac{27600 \frac{J}{mol}}{46.3 + 273.15} = 86.56 \frac{J}{mol \cdot K}$$

d. $\dfrac{0.001974}{0.007898} = \dfrac{k}{k} \left(\dfrac{0.15}{0.3}\right)^x \left(\dfrac{0.15}{0.15}\right)^y$

$0.25 = (0.5)^x$

$\dfrac{\log 0.75}{\log 0.5} = x = 2$

$\dfrac{0.25272}{2.02176} = \dfrac{k}{k} \left(\dfrac{0.6}{0.6}\right)^x \left(\dfrac{0.3}{0.6}\right)^y$

$0.125 = 0.5^y$

$\dfrac{\log 0.125}{\log 0.5} = y = 3$

$2.02176 \dfrac{M}{s} = k(0.6M)^2 (0.6M)^3$

$k = 26\ M^{-4}s^{-1}$

$rate = 26 M^{-4}s^{-1} [NO_2]^2 [CO]^3$

e. You already determined ΔH° & K for this reaction @ 25°C (problem 10)

$\Delta H^\circ = 55.8\ kJ/mol$

$K = 5.4 \times 10^{-10}$ @ 298.15 K $\ln \dfrac{K_2}{K_1} = \dfrac{\Delta H}{R} \left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

To be spontaneous, $\Delta G = 0$ & $K = 1$

$K_2 = 1$ $T_2 = ?$

$\ln \dfrac{1}{5.4 \times 10^{-10}} = \dfrac{55800}{8.314} \left(\dfrac{1}{298.15} - \dfrac{1}{T_2}\right)$

$21.34 = 6711.57 \left(0.00335 - \dfrac{1}{T_2}\right)$
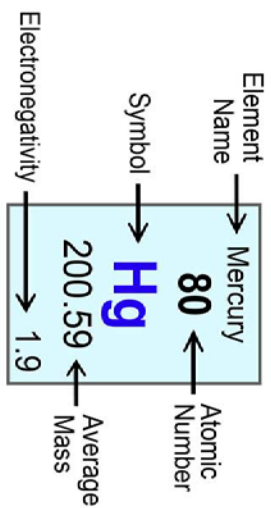
$0.0031796 = 0.00335 - \dfrac{1}{T_2}$

$\dfrac{1}{T_2} = 0.0001704$

$T_2 = 5868\ K$

Periodic Table of the Elements

Key:
Element Name → Mercury
Symbol → Hg
Atomic Number → 80
Average Mass → 200.59
Electronegativity → 1.9

> Average relative masses are to be rounded to two decimal places.
>
> All average masses are to be treated as measured quantities, and subject to significant figure rules.

Name	Z	Symbol	Avg. Mass	Electronegativity
Hydrogen	1	H	1.01	2.1
Helium	2	He	4.00	---
Lithium	3	Li	6.94	1.0
Beryllium	4	Be	9.01	1.5
Boron	5	B	10.81	2.0
Carbon	6	C	12.01	2.5
Nitrogen	7	N	14.01	3.0
Oxygen	8	O	16.00	3.5
Fluorine	9	F	19.00	4.0
Neon	10	Ne	20.18	---
Sodium	11	Na	22.99	0.9
Magnesium	12	Mg	24.31	1.2
Aluminum	13	Al	26.98	1.5
Silicon	14	Si	28.09	1.8
Phosphorus	15	P	30.97	2.1
Sulfur	16	S	32.07	2.5
Chlorine	17	Cl	35.45	3.0
Argon	18	Ar	39.95	---
Potassium	19	K	39.10	0.8
Calcium	20	Ca	40.08	1.0
Scandium	21	Sc	44.96	1.3
Titanium	22	Ti	47.88	1.5
Vanadium	23	V	50.94	1.6
Chromium	24	Cr	52.00	1.6
Manganese	25	Mn	54.94	1.5
Iron	26	Fe	55.85	1.8
Cobalt	27	Co	58.93	1.8
Nickel	28	Ni	58.69	1.8
Copper	29	Cu	63.55	1.9
Zinc	30	Zn	65.39	1.6
Gallium	31	Ga	69.72	1.6
Germanium	32	Ge	72.61	1.8
Arsenic	33	As	74.92	2.0
Selenium	34	Se	78.96	2.4
Bromine	35	Br	79.90	2.8
Krypton	36	Kr	83.80	3.0
Rubidium	37	Rb	85.47	0.8
Strontium	38	Sr	87.62	1.0
Yttrium	39	Y	88.91	1.2
Zirconium	40	Zr	91.22	1.4
Niobium	41	Nb	92.91	1.6
Molybdenum	42	Mo	95.94	1.8
Technetium	43	Tc	(98)	1.9
Ruthenium	44	Ru	101.07	2.2
Rhodium	45	Rh	102.91	2.2
Palladium	46	Pd	106.42	2.2
Silver	47	Ag	107.87	1.9
Cadmium	48	Cd	112.41	1.7
Indium	49	In	114.82	1.7
Tin	50	Sn	118.71	1.8
Antimony	51	Sb	121.76	1.9
Tellurium	52	Te	127.60	2.1
Iodine	53	I	126.90	2.5
Xenon	54	Xe	131.29	2.6
Cesium	55	Cs	132.91	0.7
Barium	56	Ba	137.33	0.9
Lutetium	71	Lu	174.97	1.1
Hafnium	72	Hf	178.49	1.3
Tantalum	73	Ta	180.95	1.5
Tungsten	74	W	183.84	1.7
Rhenium	75	Re	186.21	1.9
Osmium	76	Os	190.23	2.2
Iridium	77	Ir	192.22	2.2
Platinum	78	Pt	195.08	2.2
Gold	79	Au	196.97	2.4
Mercury	80	Hg	200.59	1.9
Thallium	81	Tl	204.38	1.8
Lead	82	Pb	207.20	1.8
Bismuth	83	Bi	208.98	1.9
Polonium	84	Po	(209)	2.0
Astatine	85	At	(210)	2.2
Radon	86	Rn	(222)	2.4
Francium	87	Fr	(223)	0.7
Radium	88	Ra	(226)	0.9
Lawrencium	103	Lr	(262)	---
Rutherfordium	104	Rf	(261)	---
Dubnium	105	Db	(262)	---
Seaborgium	106	Sg	(266)	---
Bohrium	107	Bh	(264)	---
Hassium	108	Hs	(269)	---
Meitnerium	109	Mt	(268)	---
Darmstadtium	110	Ds	(271)	---
Roentgenium	111	Rg	(272)	---
Copernicium	112	Cn	(277)	---
Ununtrium	113	Uut	(284)	---
Flerovium	114	Fl	(289)	---
Ununpentium	115	Uup	(288)	---
Livermorium	116	Lv	(293)	---
Ununseptium	117	Uus	(294)	---
Ununoctium	118	Uuo	(294)	---

*lanthanides

Name	Z	Symbol	Avg. Mass	Electronegativity
Lanthanum	57	La	138.91	1.1
Cerium	58	Ce	140.12	1.1
Praseodymium	59	Pr	140.91	1.1
Neodymium	60	Nd	144.24	1.1
Promethium	61	Pm	(145)	1.1
Samarium	62	Sm	150.36	1.2
Europium	63	Eu	151.97	1.1
Gadolinium	64	Gd	157.25	1.2
Terbium	65	Tb	158.93	1.1
Dysprosium	66	Dy	162.50	1.2
Holmium	67	Ho	164.93	1.2
Erbium	68	Er	167.26	1.2
Thulium	69	Tm	168.93	1.3
Ytterbium	70	Yb	173.04	1.1

**actinides

Name	Z	Symbol	Avg. Mass	Electronegativity
Actinium	89	Ac	(227)	1.1
Thorium	90	Th	232.04	1.3
Protactinium	91	Pa	231.04	1.5
Uranium	92	U	238.03	1.4
Neptunium	93	Np	(237)	1.4
Plutonium	94	Pu	(244)	1.3
Americium	95	Am	(243)	1.3
Curium	96	Cm	(247)	1.3
Berkelium	97	Bk	(247)	1.3
Californium	98	Cf	(251)	1.3
Einsteinium	99	Es	(252)	1.3
Fermium	100	Fm	(257)	1.3
Mendelevium	101	Md	(258)	1.3
Nobelium	102	No	(259)	1.3

	ΔH_f^0 kJ mol^{-1}	ΔG_f^0 kJ mol^{-1}
CS$_2$ (g)	116.7	67.1
CO (g)	-110.5	-137.2
CO$_2$ (g)	-393.5	-394.4

Equations

$$\Delta G = \Delta H - T\Delta S \qquad \Delta G^0 = -RTlnK \qquad \Delta G = \Delta G^o + RTlnQ$$

$$\Delta U = q + w \qquad w = -p\Delta V \qquad \Delta G = -T\Delta S_{universe}$$

$$\Delta H = C_p\Delta T \qquad ln\frac{K_2}{K_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \qquad R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

Kp = Kc (RT)$^{\Delta ngas}$ $\qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad k = Ae^{-E_a/RT}$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \qquad\qquad [A] = -kt + [A]_0 \qquad\qquad ln[A] = -kt + ln[A]_0$$