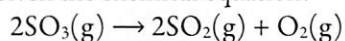# Exam 2A
Chem 1142
Spring 2019

Name: _**KEY**_

MULTIPLE CHOICE. [2 pts ea.] Record the best response on the scantron sheet. [**50 pts total.**]

Q1. Which version of the exam do you have?
A) 2A
B) 2B
C) 2C
D) 2D

Q2. Given the chemical equation:
$$2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$$
The reaction rate is equal to:
A) $+ \frac{1}{3} \Delta[SO_3]/\Delta t$
B) $+ \frac{1}{2} \Delta[SO_2]/\Delta t$
C) $-\Delta[O_2]/\Delta t$
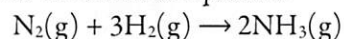D) $-\Delta[O]/\Delta t$

reactants: −ve, products: +ve   *change in conc*

$$rate = -\frac{1}{2}\frac{\Delta[SO_3]}{\Delta t} = +\frac{1}{2}\frac{\Delta[SO_2]}{\Delta t} = +\frac{1}{1}\frac{\Delta[O_2]}{\Delta t}$$

stoich. coefficients   *change in time*

Q3. Given the chemical equation:
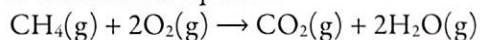$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$
If the hydrogen concentration decreases by 0.033 M over a 15.0 s period, the average rate of reaction is:
A) 0.033 M/s
B) 0.50 M/s
C) 2.2×10^{-3} M/s
D) 7.3×10^{-4} M/s

decrease in conc

$$rate = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = -\frac{1}{3} \times \frac{(-0.033M)}{15.0s} = 7.3\times10^{-4}\frac{M}{s}$$

Q4. Given the chemical equation:
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$
The rate law is:
A) impossible to determine
B) rate $= k\,[CH_4][O_2]^2$
C) rate $= k\,[CO_2][H_2O]^2$
D) rate $= \dfrac{[CO_2][H_2O]^2}{[CH_4][O_2]^2}$

must det.ⁿ experimentally (unless its an elementary step in a mechanism)

Q5. The units for the rate constant, k, for a first-order reaction are:
A) M
B) $M^{-1}\cdot s^{-1}$
C) $M\cdot s^{-1}$
D) s^{-1}

first order, power = 1

$$rate = k[A]^1 \qquad \frac{M}{S}$$
$$k = \frac{rate}{[A]}$$
$\frac{1}{S}$ M

Q6. If the rate of a reaction increases by a factor of nine when the concentration of one reactant is increased by a factor of three, the order with respect to this reactant must be:
   A) first
   B) second
   C) third
   D) sixth

Handwritten: 1st order, rate $\propto [A]^1$ | 2nd order, rate $\propto [A]^2$ | 3rd order, rate $\propto [A]^3$

$[A]_1$ $[A]_2$ rate increase
1 3 $3^1 = 3$
1 3 $3^2 = 9$ ✓
1 3 $3^3 = 27$

Q7. A plot of ln [A] vs time is linear for the reaction: A → B. This information can be used to determine:
   A) the reaction is zeroth order with respect to A
   B) the reaction is first order with respect to A
   C) the reaction is second order with respect to A
   D) the slope of the graph is equal to $-E_A/R$

*Handwritten:* 1st order: $\ln[A]_t = -Kt + \ln[A]_0$ $y = mx + b$

Q8. A first order reaction takes 12 seconds for the concentration of A (the reactant) to decrease from 1.0 M to 0.50 M. How long will it take for the concentration to decrease from 1.0 M to 0.25 M?
   A) 6.0 s
   B) 12 s
   C) 24 s
   D) 48 s

Handwritten: 1st order, $t_{\frac{1}{2}} = \frac{0.693}{K}$ (constant)

$1.0M \xrightarrow{\times t_{\frac{1}{2}}, \times t_{\frac{1}{2}}} 0.25M$ two half-lives
$\Rightarrow t = 2 \times t_{\frac{1}{2}} = 2 \times 12s = 24s$

Q9. The highest point on an energy vs. reaction progress plot is called the:
   A) transition state
   B) reaction intermediate
   C) frequency factor
   D) degree of exothermicity

Handwritten: transition state (transition between R → P)
E, R, E_a, P, Reaction progress
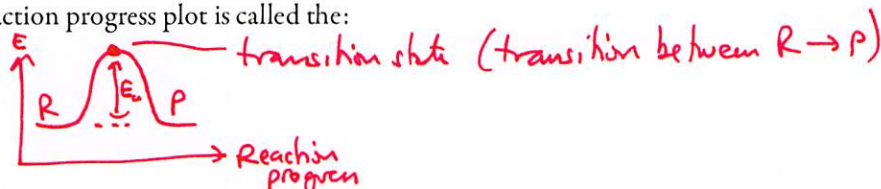
Q10. In general, reactions speed up with increasing temperature. This is primarily due to the fact that increasing temperature...
   A) increases the reactant concentrations
   B) increases the frequency of collisions
   C) increases the probability of a collision with $E \geq E_A$
   D) increases the probability of a collision with a successful orientation

Handwritten: exponential increase: $e^{-E_a/RT} \propto e^{-E_a/RT}$ T

Q11. What type of plot can be used to determine the activation energy for a reaction?
   A) ln [A] vs. t
   B) 1 / [A] vs. t
   C) 1 / k vs. 1 / T
   D) ln (k) vs. 1 / T

Handwritten: Arrhenius plot
$\ln K = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A$
$y = m \cdot x + b$ slope $= -\frac{E_a}{R}$

Q12. The chemical equation, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ is postulated to occur via the mechanism:
   i) $N_2(g) \rightarrow 2N(g)$ *slow*
   ii) $2N(g) + H_2(g) \rightarrow N_2H_2(g)$ *fast*
   iii) $N_2H_2(g) + 2H_2(g) \rightarrow 2NH_3(g)$ *fast*
   What should the rate law be?
   A) rate = $k [N_2][H_2]^3$
   B) rate = $k [N_2]$
   C) rate = $k [N]^2$
   D) rate = $k [N_2H_2][H_2]^2$

Handwritten: Rate determining/limiting step.
conc of reactants colliding
for elementary steps, rate = $k \times [\ ] \times [\ ] \times \ldots$

Q13. What is the molecularity of the elementary step: $N_2(g) \longrightarrow 2N(g)$?
  A) unimolecular
  B) bimolecular
  C) termolecular
  D) quadmolecular

1 species colliding

Q14. Catalysts work by:
  A) lowering $\Delta H°_{rxn}$
  B) lowering the collision frequency
  C) lowering the concentration of intermediates
  D) lowering the activation energy

Q15. The chemical equilibrium, $MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$, has an equilibrium constant of 3.2×10^{-10} at room temperature. At this temperature, an equilibrium mixture should consist of:
  A) mainly CO_2 and MgO, with small amounts of $MgCO_3$
  B) mainly $MgCO_3$, with small amounts of MgO and CO_2
  C) an equal mixture of $MgCO_3$, MgO, and CO_2
  D) An equal mixture of MgO and $MgCO_3$. with a small amount of CO_2

K is small
⇒ mainly R
few P
@ eqⁿ !

Q16. The reaction, $A(g) \rightleftharpoons 2B(g)$ has an equilibrium constant of 100. Predict the equilibrium constant for the reaction, $B(g) \rightleftharpoons ½ A(g)$
  A) 10
  B) –50
  C) 0.1
  D) –25

reverse , halve
(×¹/K) (∧½)
$100 \xrightarrow{invert} \frac{1}{100} \xrightarrow{∧½} \frac{1}{10} = 0.1$

Q17. For which equilibrium reaction will K_p always equal K_c?
  A) $H_2(g) + O_2(g) \rightleftharpoons H_2O_2(l)$
  B) $N_2(g) + O_2(g) \rightleftharpoons 2NO(l)$
  C) $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$
  D) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$K_p = K_c (RT)^{\Delta n_g}$ *change in #mol gas*
if $\Delta n_g = 0$, $K_p = K_c$
2 mol gas → 2 mol gas, $\Delta n_g = 0$

Q18. For the equilibrium,
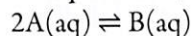 $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$
  the partial pressures of gases above pure carbon are 0.010 atm (O_2) and 4.3 atm (CO) at 23 °C. What is K_p equal to?
  A) 0.043
  B) 4300
  C) 8.61
  D) 1800
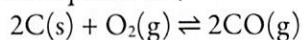
$K_p = \frac{(P_{CO})^2}{(P_{O_2})} = \frac{4.3^2}{0.010} = 1849 = 1800 \,(2s.f.)$

Q19. For the equilibrium,
  $2A(aq) \rightleftharpoons B(aq)$
  if we start out with $[A] = 1.00$ M and $[B] = 0.00$ M, and end up with $[A] = 0.80$ M at equilibrium, what must the equilibrium constant, K_c, be?
  A) 0.16
  B) 0.25
  C) 0.31
  D) 0.80

$2A \rightleftharpoons B$
I	1.00	0.00
C	−2x	+x
E	(1.00−2x)	(x)
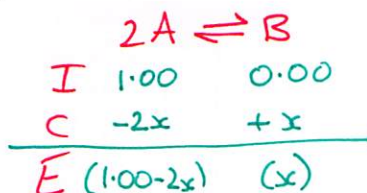
0.80M ⇒ 1.00−2x = 0.80
⇒ 2x = 1.00−0.80 = 0.20
⇒ x = 0.20/2 = 0.10

$⇒ [A]_{eq} = 0.80M, \quad [B]_{eq} = x = 0.10M, \quad K_c = \frac{[B]_{eq}}{[A]_{eq}^2} = \frac{0.10}{(0.80)^2}$

0.16 (2sf)
"

Q20. Given the equilibrium,
$$NO(g) + H_2(g) \rightleftharpoons H_2NO(g)$$
which has an equilibrium constant, $K_p = 0.40$ at room temperature, predict the direction the reaction will proceed to reach dynamic equilibrium if $p_{NO} = 0.10$ atm, $p_{H_2} = 0.20$ atm, and $p_{H_2NO} = 0.10$ atm.
A) will shift to the left
B) will not shift—already at equilibrium
C) will shift to the right
D) not possible to determine the shift
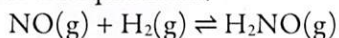
$$Q_p = \frac{(P_{H_2NO})}{(P_{NO})(P_{H_2})} = \frac{0.10}{0.10 \times 0.20} = 5.0$$

$Q_p > K_p$, so Q_p must $\downarrow$ to reach K_p!

$Q_p = \frac{(P_{H_2NO}) \downarrow}{(P_{NO})(P_{H_2}) \uparrow}$

$\Rightarrow$ shift to LHS

Q21. Given the equilibrium,
$$NO(g) + H_2(g) \rightleftharpoons H_2NO(g) \quad ; \Delta H°_{rxn} = -34.0 \text{ kJ}$$
Predict the direction of shift if the concentration of $H_2(g)$ is decreased
A) will shift to the left
B) will neither shift left nor right
C) will shift to the right
D) not possible to determine the shift (must use an ICE-chart)

stress!

relief: $[H_2]\uparrow$, so shift to LHS to make more!

Q22. Given the equilibrium,
$$NO(g) + H_2(g) \rightleftharpoons H_2NO(g) \quad ; \Delta H°_{rxn} = -34.0 \text{ kJ}$$
Predict the direction of shift if the total volume is decreased
A) will shift to the left
B) will neither shift left nor right
C) will shift to the right
D) not possible to determine the shift (must use an ICE-chart)

$V\downarrow \Rightarrow P\uparrow$ (Boyle's law)
$\Rightarrow$ stress: $P\uparrow$
relief: $P\downarrow \Rightarrow$ shift to RHS to make fewer gas molecules, which will lower pressure.

Q23. Given the equilibrium,
$$NO(g) + H_2(g) \rightleftharpoons H_2NO(g) \quad ; \Delta H°_{rxn} = -34.0 \text{ kJ}$$
Predict the direction of shift if the reaction temperature is decreased
A) will shift to the left
B) will neither shift left nor right
C) will shift to the right
D) not possible to determine the shift (must use an ICE-chart)

$-T\downarrow$, remove heat (stress)
relief: make heat
exothermic: $A \rightleftharpoons B + \text{heat} \Rightarrow$ shift to RHS

Q24. When forming the expression for an equilibrium constant, what substances have an effective concentration/pressure of one (1)?
A) pure solids
B) aqueous solutes
C) gases
D) elements

pure solids
pure liquids } effective $[\,]$, $p = 1$

Q25. In the Arrhenius equation, the pre-exponential factor, A, is often written as a product of two other factors: $A = p \times Z$. The factor "Z" represents the collision frequency. What does the factor "p" represent?
A) The probability of a collision with $E \geq E_A$
B) The probability of a collision with proper orientation
C) The probability of a collision with a catalyst
D) The probability of a collision with $E \geq \Delta H°_{rxn}$

Short Response.

Show ALL work to receive credit.

Q26. [12 pts.] A chemist is trying to determine the rate law for a reaction between $H_2(g)$ and $NO(g)$. The chemical equation is:

$$H_2(g) + 2NO(g) \longrightarrow N_2(g) + H_2O_2(g)$$
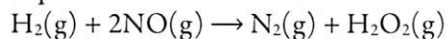
The chemist decides to use the method of initial rates, whereby different experiments are carried out with different initial concentrations, and the rate at the beginning of the experiment is measured. The collected data looks like:

Experiment #	$[H_2]$ / M	$[NO]$ / M	initial rate / $M \cdot s^{-1}$
1	0.10	0.20	3.2×10^{-5}
2	0.20	0.20	1.28×10^{-4}
3	0.10	0.35	3.2×10^{-5}

From this data, determine the rate law, showing all work.

Assume: $rate = K[H_2]^m[NO]^n$

$$\frac{rate\,(2)}{rate\,(1)} = \frac{K[0.20M]^m[0.20M]^n}{K[0.10M]^m[0.20M]^n} \Rightarrow \frac{1.28\times10^{-4}M\cdot s^{-1}}{3.2\times10^{-5}M\cdot s^{-1}} = 4.0 = 2.0^m \Rightarrow m=2 \text{ (by inspection)}$$

$$\frac{rate\,(3)}{rate\,(1)} = \frac{K[0.10M]^m[0.35M]^n}{K[0.10M]^m[0.20M]^n} \Rightarrow \frac{3.2\times10^{-5}M\cdot s^{-1}}{3.2\times10^{-5}M\cdot s^{-1}} = 1.0 = 1.75^n \Rightarrow n=0 \text{ (by inspection)}$$

$$\Rightarrow rate = K[H_2]^2$$

What is the overall order of this reaction? __2__

What is the value of the rate constant, including units? __$3.2\times10^{-3}M^{-1}s^{-1}$__

$$K = \frac{rate}{[H_2]^2}, \quad trial\ 1: \quad K = \frac{3.2\times10^{-5}M\cdot s^{-1}}{[0.10M]^2} = 3.2\times10^{-3}\ M^{-1}s^{-1}$$

second order.

Q27. [13 pts.]   The chemical equation: $A(g) \longrightarrow B(g)$ is found to have a rate law, *rate = k* $[A]^2$.

i)   If the initial concentration of A is 0.25 M, and the rate constant is 0.011 $M^{-1}s^{-1}$, calculate how long it will take for the concentration to reach 0.0025 M.

2nd order: $\quad \dfrac{1}{[A]_t} = Kt + \dfrac{1}{[A]_0} \quad \Rightarrow \quad t = \dfrac{\dfrac{1}{[A]_t} - \dfrac{1}{[A]_0}}{k} = \dfrac{\dfrac{1}{0.0025M} - \dfrac{1}{0.25M}}{0.011\ M^{-1}s^{-1}}$

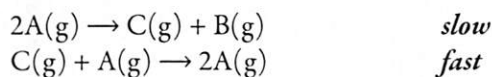$= \dfrac{396\ M^{-1}}{0.011\ M^{-1}s^{-1}} = 36,000\ s \quad (2sf.)$

because $[A]_0$ decreases over time

ii)   What happens to the half-life for this reaction over time? Explain.

$t_{\frac{1}{2}} = \dfrac{1}{[A]_0 K}$,   so $t_{\frac{1}{2}} \propto \dfrac{1}{[A]_0} \Rightarrow$ for every $t_{\frac{1}{2}}$ that passes, $\dfrac{1}{[A]_0} \uparrow$

$\Rightarrow t_{\frac{1}{2}} \uparrow$ over time!

iii) A possible mechanism for the reaction is given below:

$2A(g) \longrightarrow C(g) + B(g) \qquad\qquad$ *slow*
$C(g) + A(g) \longrightarrow 2A(g) \qquad\qquad$ *fast*

Is this mechanism consistent with the rate law given at the beginning of this problem? What can you conclude (if anything) about this mechanism?

from mech: slow step = overall rate = $K[A]^2$

- consistent with xpt rate law above.

- however, this does <u>not</u> <u>prove</u> mechanism is correct.
   - could just be a coincidence!

(but... if mechanism give inconsistent rate law, we could disprove mechanism!)

Q28. [12 pts.]   **Using complete and grammatically correct sentences, answer the following questions:**

i) What is meant by the term: heterogenous catalyst?

A catalyst that is in a _different phase_ as the reactants.
(A catalyst is a substance that speeds up a reaction without being consumed)

ii) What is a reaction intermediate?

A substance that is neither a reactant, nor a product, of the overall, stoichiometric chemical equation.

iii) What is an "Arrhenius plot?"

A graph of $\ln(k)$ vs. $\frac{1}{T}$. Its slope is $\frac{-E_a}{R}$, so the activation energy can be determined by: $E_a = slope \times -R$

Give mathematical expressions for the following:

iv) Write the expression for K_c for the equilibrium:

$$H_2SO_4(aq) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + SO_4^{2-}(aq)$$
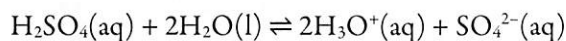
$$K_c = \frac{[H_3O^+]^2[SO_4^{2-}]}{[H_2SO_4]}_{eq}$$

v) Write the expression for K_p for the equilibrium

$$2NO_2(g) + 2H_2(g) \rightleftharpoons HNO_3(g) + NH_3(g) + \tfrac{1}{2}O_2(g)$$

$$K_p = \frac{(P_{HNO_3})(P_{NH_3})(P_{O_2})^{1/2}}{(P_{NO_2})^2(P_{H_2})^2}_{eq}$$

(note... [ ] means _molar conc_ !)

Q29. [13 pts.] The chemical reaction,

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

has an equilibrium constant, $K_p = 64.0$ at 23 °C.

$$Q_p = \frac{(P_{HBr})^2}{(P_{H_2})(P_{Br_2})} = 1.00$$

$Q_p < K_p$, so will shift to RHS!

If the initial pressure of all three gases (H_2, Br_2, and HBr) is 0.250 atm, calculate the final equilibrium pressures of each gas.

$$H_2 + Br_2 \rightleftharpoons 2HBr$$

I	0.250	0.250	0.250
C	$-x$	$-x$	$+2x$
E	$(0.250-x)$	$(0.250-x)$	$(0.250+2x)$

(shift to RHS, since $Q < K$)
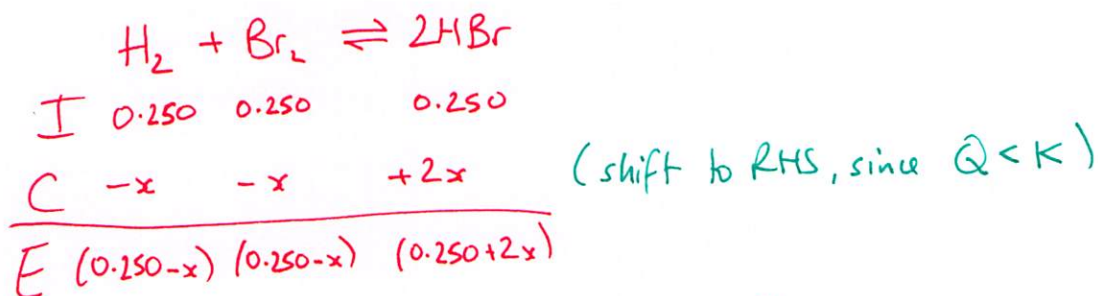
$$K_p = \frac{(P_{HBr})^2}{(P_{H_2})(P_{Br_2})} \implies 64.0 = \frac{(0.250+2x)^2}{(0.250-x)(0.250-x)}$$

perfect square!

$$\implies \sqrt{64.0} = 8.00 = \frac{0.250+2x}{0.250-x}$$

$$\implies 8.00(0.250-x) = 0.250+2x$$

$$\implies 2.00 - 8.00x = 0.250 + 2x$$

$$\implies 10.00x = 1.75$$

$$\implies x = \frac{1.75}{10.00} = 0.175$$

So, $P_{HBr} = (0.250+2x) = 0.600$ atm
$P_{H_2} = P_{Br_2} = 0.250-x = 0.075$ atm $\Big\}$ 3 d.p.)

BONUS Question:

What is the name given to the slowest step in a reaction mechanism?

Rate determining (or limiting) step

- 8 -

𝒰seful Information

Periodic Table of the Elements

IA 1	IIA 2	3	4	5	6	7	8	9	10	11	12	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	VIIIA 18
1 **H** 1.01																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.87	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92160	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** [98]	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba*** 137.33	71 **Lu** 174.97	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.20	83 **Bi** 208.98	84 **Po** [210]	85 **At** [210]	86 **Rn** [222]
87 **Fr** [223]	88 **Ra**** [226]	103 **Lr** [262]	104 **Rf** [261]	105 **Db** [262]	106 **Sg** [266]	107 **Bh** [264]	108 **Hs** [265]	109 **Mt** [268]	110 [269]	111 [272]	112 [277]	113	114 [285]	115	116 [289]	117	118 [293]

57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** [145]	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04
89 **Ac** [227]	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** [237]	94 **Pu** [244]	95 **Am** [243]	96 **Cm** [247]	97 **Bk** [247]	98 **Cf** [251]	99 **Es** [252]	100 **Fm** [257]	101 **Md** [258]	102 **No** [259]

$$R = 8.3145 \frac{J}{mol \cdot K} = 0.08206 \frac{atm \cdot L}{mol \cdot K}$$

$$k = Ae^{-\frac{E_A}{RT}} \qquad \ln k = -\frac{E_A}{R}\cdot\frac{1}{T} + \ln A \qquad \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

- **0-order:** $[A]_t = -kt + [A]_0 \qquad\qquad t_{1/2} = \dfrac{[A]_0}{2k}$

- **1-order:** $\ln[A]_t = -kt + \ln[A]_0 \qquad \ln\left(\dfrac{[A]_t}{[A]_0}\right) = -kt \qquad t_{1/2} = \dfrac{0.693}{k}$

- **2-order:** $\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0} \qquad\qquad t_{1/2} = \dfrac{1}{[A]_0 k}$

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

Given: $ax^2 + bx + c = 0$, then $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$