

Exam 2A

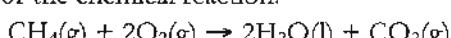
Chem 1142

Spring 2015

Name: KEY

MULTIPLE CHOICE. [4 pts ea.] Choose the best response on the scantron sheet. [60 pts total.]

Q1. For the chemical reaction:



which of the following expressions would correspond to the rate of the reaction?

- a) $\frac{\Delta[\text{CH}_4]}{\Delta t}$ b) $\frac{\Delta[\text{O}_2]}{\Delta t}$ c) $\frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$ d) $\frac{\Delta[\text{CO}_2]}{\Delta t}$

$$\text{rate} = -\frac{\Delta[\text{CH}_4]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{O}_2]}{\Delta t} = +\frac{1}{2} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = +\frac{\Delta[\text{CO}_2]}{\Delta t}$$

Q2. A set of experiments reveals that when the initial concentration of a reactant A is increased by a factor of 4, the initial rate of the reaction is unaffected. From this information we can determine that the reaction order with respect to A is:

- a) Zero b) One c) Two d) Three e) Four

if $\text{rate} \propto [\text{A}]^n$
 $\propto 1$

Q3. The units for a second-order rate constant are:

- a) s^{-1} b) M/s c) M^2/s d) $\text{M}^{-1}\text{s}^{-1}$ e) M^3s^{-2}

then $[\text{A}]$ doesn't affect rate.

Q4. For the reaction: $\text{A} \rightarrow 2\text{B}$, a plot of $[\text{A}]^{-1}$ vs. t is linear. This allows us to determine:

- a) The reaction must be zero-order with respect to A
 b) The reaction must be first-order with respect to A
 c) The reaction must be second-order with respect to ~~A~~
 d) The activation energy is equal to the slope of the graph $\times -R$
 e) The reaction is an elementary reaction

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

Δn_g ↘ # molecules of gas products
(+) # molecules of gas reactants

Q5. In which equilibrium reaction below will $K_p = K_c$?

- a) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{l})$ b) $\text{HCl}(\text{g}) + \text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaCl}_2(\text{s}) + \text{CO}_2(\text{g})$ $\Delta n_g = 0 \Rightarrow K_p = K_c$
 c) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ d) $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$
 e) $\text{CH}_3\text{OH}(\text{l}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{CH}_2\text{O}(\text{l}) + \text{H}_2(\text{g})$

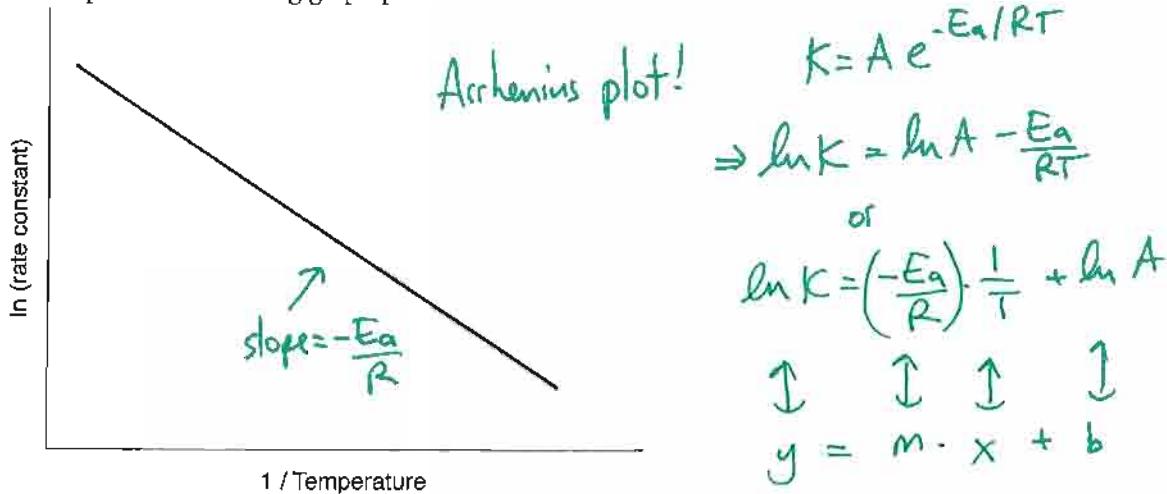
Q6. If K_c for the reaction: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ is 12.0 at 25 °C, then predict the equilibrium constant for the reaction: $4\text{NH}_3(\text{g}) \rightleftharpoons 2\text{N}_2(\text{g}) + 6\text{H}_2(\text{g})$ at the same temperature.

- a) 12.0 b) 24.0 c) -0.0908 d) -24.0 e) 0.00694

reverse rxn, invert K
 double rxn, square K

$$\Rightarrow \text{new } K = \left(\frac{1}{12.0} \right)^2 = \frac{1}{144}$$

Q7. The slope of the following graph provides information about:



- a) The value of ΔH°
- b) The rate constant, assuming a first-order reaction
- c) The rate constant, assuming a second-order reaction
- d) The activation energy
- e) The molecularity of the elementary reaction

Q8. The reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$ is thought to proceed via the mechanism:



Predict the rate law for this reaction.

- a) rate $\approx k[H_2][I_2]$
- b) rate $= k[HI]^2$
- c) rate $= k[H_2]$
- d) rate $= k[I_2]$
- e) rate $= k[I][H_2]$

Q9. Given the reaction: $2N_2O(g) \rightleftharpoons 2NO(g) + N_2(g); \Delta H^\circ = -130 \text{ kJ/mol}$ at 25°C , predict in which direction the equilibrium will shift after the temperature is decreased.

- a) To the left
- b) No change
- c) To the right
- d) Not enough information to predict



Q10. If the reaction quotient is equal to the equilibrium constant, then:

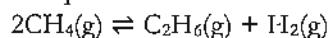
- a) The reaction will proceed to make more reactants, until it reaches equilibrium
- b) The reaction is at equilibrium
- c) The reaction will proceed to make more products, until it reaches equilibrium
- d) If the reaction is exothermic, it will proceed to make more products
- e) If the reaction is endothermic, it will proceed to make more products

lower T, remove heat
(stress)
 $\Rightarrow \text{heat} = \text{make heat}$

Short Response.

Show ALL work to receive credit.

Q11. [20 pts.] The chemical equilibrium:



has a equilibrium constant, K_p , equal to 0.092 at 120 °C. Imagine you started with a mixture of gases where the partial pressure of CH_4 is 0.10 atm and the partial pressures of C_2H_6 and H_2 are both 1.0 atm.

a) Calculate the reaction quotient, and explain which direction the reaction will shift in order to come to equilibrium.

$$Q_p = \frac{P_{\text{C}_2\text{H}_6} \times P_{\text{H}_2}}{P_{\text{CH}_4}^2} = \frac{1.0 \times 1.0}{0.10^2} = 100$$

$Q_p > K_p \Rightarrow$ will shift to LHS
to reduce Q_p , until it equals K_p .

b) Calculate the equilibrium partial pressures of all three gases, as well as the total pressure.



| | | | | |
|---|-----------|---------|---------|----------------|
| I | 0.10 atm | 1.0 atm | 1.0 atm | |
| C | +2x | -x | -x | (shift to LHS) |
| E | (0.10+2x) | (1.0-x) | (1.0-x) | |

$$K_p = \frac{P_{\text{C}_2\text{H}_6} \times P_{\text{H}_2}}{P_{\text{CH}_4, \text{eq}}^2} \Rightarrow 0.092 = \frac{(1-x)^2}{(0.10+2x)^2}$$

perfect square!

$$\Rightarrow \sqrt{0.092} = 0.303 = \frac{1-x}{0.10+2x}$$

$$\Rightarrow 0.303(0.10+2x) = 1-x$$

$$\Rightarrow 0.0303 + 0.606x = 1-x$$

$$\Rightarrow 1.606x = 0.9697$$

$$\Rightarrow x = \frac{0.9697}{1.606} = 0.6038$$

$$\Rightarrow \left. \begin{array}{l} P_{\text{CH}_4} = 0.10+2x = 1.31 \text{ atm} \\ P_{\text{C}_2\text{H}_6} = P_{\text{H}_2} = 1-x = 0.4 \text{ atm} \end{array} \right\} P_{\text{tot}} = P_{\text{CH}_4} + P_{\text{C}_2\text{H}_6} + P_{\text{H}_2} = \boxed{2.1 \text{ atm}}$$

Q12. [20 pts.] Given the following information, deduce the rate law and the value of the rate constant for the following reaction: $A + 2B \rightarrow 3C$

Be sure to show *all* work. If you adopt the inspection method, be sure to explain how you determine the reaction orders using complete sentences.

| Experiment | $[A]_0 / M$ | $[B]_0 / M$ | Initial rate / $M \cdot s^{-1}$ |
|------------|-------------|-------------|---------------------------------|
| #1 | 0.50 | 0.25 | 3.7×10^{-3} |
| #2 | 0.50 | 0.35 | 5.18×10^{-3} |
| #3 | 1.0 | 0.25 | 1.48×10^{-2} |

$$\text{Rate} = K[A]^x[B]^y$$

$$\frac{\text{rate}(3)}{\text{rate}(1)} = \frac{1.48 \times 10^{-2} \text{ M/s}}{3.7 \times 10^{-3} \text{ M/s}} = 4.0 = \frac{K[1.0 \text{ M}]^x[0.25 \text{ M}]^y}{K[0.50 \text{ M}]^x[0.25 \text{ M}]^y} = \frac{[1.0 \text{ M}]^x}{[0.50 \text{ M}]^x} = \frac{(1.0 \text{ M})^x}{(0.50 \text{ M})^x} = 2.0^x \Rightarrow x=2$$

$$\frac{\text{rate}(2)}{\text{rate}(1)} = \frac{5.18 \times 10^{-3} \text{ M/s}}{3.7 \times 10^{-3} \text{ M/s}} = 1.4 = \frac{K[0.50 \text{ M}]^x[0.35 \text{ M}]^y}{K[0.50 \text{ M}]^x[0.25 \text{ M}]^y} = 1.4^y \Rightarrow y=1$$

$$K = \frac{\text{Rate}}{[A]^x[B]^y} \Rightarrow \text{rate} : K = \frac{1.48 \times 10^{-2} \text{ M} \cdot \text{s}^{-1}}{(1.0 \text{ M})^2[0.25 \text{ M}]^1} = 0.0592 \text{ M}^{-2} \text{s}^{-1}$$

rate law: $\text{rate} = K[A]^2[B]$

rate constant: $K = 0.0592 \text{ M}^{-2} \text{s}^{-1}$ (include units)

Q13. [10 pts.] a) K_c for the reaction: $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ is equal to 13.9 at 45 °C. Calculate K_p at this same temperature.

$$\Delta n_g = 1 - 2 = -1$$
$$T = 45 + 273 \text{ K} = 318 \text{ K}$$
$$K_p = K_c (RT)^{\Delta n_g}$$
$$\Rightarrow K_p = 13.9 \times (0.08206 \frac{\text{atm}}{\text{mol} \cdot \text{K}})^{-1} = 0.532$$

note: since we're converting $\frac{\text{mol}}{\text{L}}$ \rightarrow atm, we
use the $0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}}$ value of R.
↓
units? K_p and K_c are dimensionless!

[10 pts.] b) Using complete sentences, explain how it is possible to tell whether a reaction is exothermic or endothermic by measuring how the equilibrium constant changes as the reaction temperature is increased.

For an exothermic rxn, heat is given off, and
so the chemical eqⁿ is:



If we increase the temperature, this is analogous to adding heat, causing a stress.

Le Chatelier's principle says that the eqⁿ will shift to try & relieve this stress, therefore will cause eqⁿ to shift to LHS. Since $K_c = \frac{[\text{B}]}{[\text{A}]}$, K_c will decrease as temp is increased for an exothermic rxn.

Not: since "heat" doesn't enter into expression for K_c , this shift will affect the value of K!

for similar reasons, endothermic rxns suffer an increase in K as temp is increased!



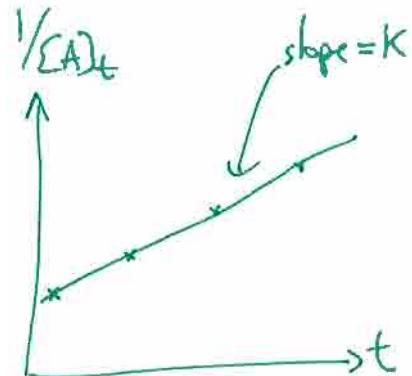
increase T (stress), will cause shift to RHS to (adding heat) remove heat, $\Rightarrow K$ increases!

Bonus Question: Given a chemical reaction, $A \rightarrow P$, what would you have to plot to determine whether the reaction was *second order* with respect to A? Sketch this graph, and explain how you would use it to determine the second order rate constant.

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

$\uparrow \quad \uparrow \quad \uparrow \uparrow$

$$y = b + mx$$



"This is a lovely old song that tells of a young woman who leaves her cottage, and goes off to work. She arrives at her destination, and places some solid NH_4HS in a flask containing 0.50 atm of ammonia, and attempts to determine the pressures of ammonia and hydrogen sulfide when equilibrium is reached."

U

useful Information

Periodic Table of the Elements

| IA | IIA | | | | | | | | | | | | | IIIA | IVA | VA | VIA | VIIA | VIIIA | | |
|--------------------|---------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|------------------------|--------------------|-------------------|--------------------|-------------------|-------------------|--|--|
| 1 H 1.01 | 2 Be 9.01 | | | | | | | | | | | | | | | | | 16 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 16.90 | 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 | | |
| 18 K 39.10 | 19 Ca 40.08 | 20 Sc 44.96 | 21 Tl 47.87 | 22 V 50.94 | 23 Cr 52.00 | 24 Mn 54.94 | 25 Fe 55.85 | 26 Co 56.93 | 27 Ni 58.69 | 28 Cu 63.55 | 29 Zn 65.39 | 30 Ga 69.72 | 31 Ge 72.61 | 32 As 74.92 [60] | 33 Se 78.95 | 34 Br 79.90 | 35 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 116.71 | 51 Sb 121.76 | 52 Te 127.80 | 53 I 128.90 | 54 Xe 131.29 | | | | |
| 55 Cs 132.91 | 56 Ba* 137.33 | 57 Lu 174.97 | 58 Hf 176.40 | 59 Ta 180.95 | 60 W 183.84 | 61 Re 186.21 | 62 Os 190.23 | 63 Ir 192.22 | 64 Pt 195.08 | 65 Au 196.97 | 66 Hg 200.58 | 67 Tl 204.38 | 68 Pb 207.20 | 69 Bi 208.98 | 70 Po [210] | 71 At [210] | 72 Rn [220] | | | | |
| 87 Fr [221] | 88 Ra** [226] | 89 Lr [231] | 90 Rf [232] | 91 Db [262] | 92 Sg [264] | 93 Bh [265] | 94 Hs [266] | 95 Mt [268] | 96 Dy [272] | 97 Ho [273] | 98 Er [285] | 99 Tm [289] | 100 Yb [293] | | | | | | | | |
| | | 57 La 138.91 | 58 Ce 140.12 | 59 Pr 140.91 | 60 Nd 144.24 | 61 Pm 145.91 | 62 Sm 150.36 | 63 Eu 151.98 | 64 Gd 157.25 | 65 Tb 158.92 | 66 Dy 162.50 | 67 Ho 164.93 | 68 Er 167.20 | 69 Tm 168.95 | 70 Yb 173.04 | | | | | | |
| | | 69 Ac [227] | 70 Th 232.04 | 71 Pa 231.04 | 72 U 238.03 | 73 Np [237] | 74 Pu [244] | 75 Am [243] | 76 Cm [247] | 77 Bk [247] | 78 Cf [251] | 79 Es [262] | 80 Fm [257] | 81 Md [258] | 82 No [259] | | | | | | |

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

$$k = A e^{-\frac{E_A}{RT}}$$

$$\ln k = -\frac{E_A}{R} \cdot \frac{1}{T} + \ln A$$

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

• 0-order: $[A]_t = -kt + [A]_0$

$$t_{1/2} = \frac{[\text{A}]_0}{2k}$$

• 1-order: $\ln[A]_t = -kt + \ln[A]_0$

$$\ln\left(\frac{[\text{A}]_t}{[\text{A}]_0}\right) = -kt$$

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

• 2-order: $\frac{1}{[\text{A}]_t} = kt + \frac{1}{[\text{A}]_0}$

$$t_{1/2} = \frac{1}{[\text{A}]_0 k}$$

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

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