version: 455

$\mathsf{Exam}\ 3\ -\ \mathsf{S23}\ -\ \mathsf{McCord}\ -\ \mathsf{ch302}$

last name

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1]																2
H 1.008	2											13	14	15	16	17	He 4.003
3	4]										5	6	7	8	9	10
Li	Be											В	С	N	0	F	Ne
6.941	9.012											10.81	12.01	14.01	16.00	19.00	20.18
11	12											13	14	15	16	17	18
Na	Mg		4	-	0	7	0	0	10		10	AI	Si	P	S	CI	Ar
22.99	24.31	3	4	5	6	7	8	9	10	11	12	26.98	28.09	30.97	32.07	35.45	39.95
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.10	40.08	44.96	47.87	50.94	52.00	54.94	55.85	58.93	58.69	63.55	65.38	69.72	72.64	74.92	78.96	79.90	83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Υ	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те		Xe
85.47	87.62	88.91	91.22	92.91	95.94	(98)	101.07	102.91	106.42	107.87	112.41	114.82	118.71	121.76	127.60	126.90	131.29
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Hf	Та	W	Re	Os	lr	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
132.91	137.33	138.91	178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59	204.38	207.20	208.98	(209)	(210)	(222)
87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	FI	Mc	Lv	Ts	Og
(223)	(226)	(227)	(267)	(268)	(269)	(270)	(270)	(278)	(281)	(282)	(285)	(286)	(289)	(290)	(293)	(294)	(294)

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm	62 Sm 150.36	63 Eu	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	71 Lu 174.97
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	NO	Lr
232.04	231.04	238.03	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(266)

constants
R = 0.08206 L atm/mol K
R=0.08314L bar/mol K
R = 62.36 L Torr/mol K
R=8.314L kPa/mol K
$R=8.314~{\rm J/mol~K}$
$N_{\rm A}=6.022\times 10^{23}~/{\rm mol}$

<u>conversions</u>

1 atm = 760 torr 1 atm = 14.7 psi 1 atm = 101325 Pa 1 atm = 1.01325 bar 1 bar = 10^5 Pa °F = °C(1.8) + 32 K = °C + 273.15

conversions

1 in = 2.54 cm
1 ft = 12 in
1 yd = 3 ft
1 mi = 5280 ft
1 lb = 453.6 g
1 ton = 2000 lbs
1 tonne = 1000 kg
1 gal = 3.785 L
$1 \text{ gal} = 231 \text{ in}^3$
1 gal = 128 fl oz
$1~{\rm fl~oz}=29.57~{\rm mL}$
1 Troy oz $=31.104~{\rm g}$

water data
$C_{\rm s,ice} = 2.09~\rm J/g~^\circ C$
$C_{\rm s,water} = 4.184 \text{ J/g} \circ \text{C}$
$C_{\rm s,steam} = 2.03 \ {\rm J/g} \ ^{\circ}{\rm C}$
$\rho_{\rm water} = 1.00~{\rm g/mL}$
$\rho_{\rm ice}=0.9167~{\rm g/mL}$
$\rho_{\rm seawater} = 1.024~{\rm g/mL}$
$\Delta H_{\rm fus} = 334~{\rm J/g}$
$\Delta H_{\rm vap} = 2260~{\rm J/g}$
$k_{\rm f} = 1.86 \ ^{\circ}{\rm C}/m$
$k_{\rm b}=0.512~{\rm ^\circ C}/m$

This exam should have exactly 25 questions. Each question is equally weighted at 4 points each. You will enter your answer choices on the virtual bubblehseet after you have finished. Your score is based on what you submit on the virtual bubblesheet and not what is circled on the exam.

1. The reaction $NO_2 + CO \rightarrow NO + CO_2$ is found to obey the following empirical rate law:

$$rate = k[NO_2][CO]$$

For this reaction, if you start with an initial concentration of CO that is much higher than the initial concentration of NO₂ ($[CO]_0 >> [NO_2]_0$) then a plot of $\ln[NO_2]$ will appear

- a. linear with zero slope as the kinetics are now zero order in CO.
- b. linear as the kinetics are now pseudo-1st order in NO_2 .
 - c. curved as the kinetics are 1st order in NO_2 .
 - d. curved as the kinetics are 2nd order overall for the reaction.

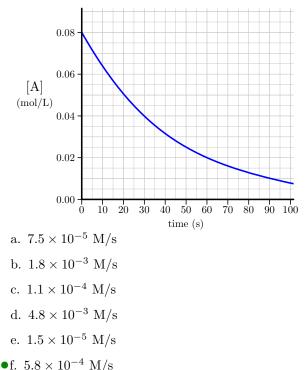
Explanation: the kinetics are 1st order in NO₂, and the conc of CO is so high that it effectively doesn't change thus making the reaction pseudo first order in NO₂. This means that the plot of $\ln[NO_2]$ will be linear.

2. The Statue of Liberty, constructed mostly from copper, has corroded over time to develop a lovely bluish-green patina. One of the chemicals responsible for this patina is Cu(OH)₂ ($K_{sp} = 2.2 \times 10^{-20}$). What is its molar solubility?

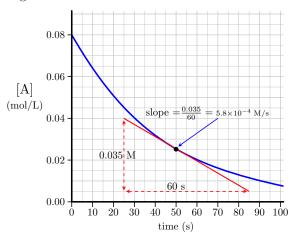
a. $6.7 \times 10^{-17} \text{ mol/L}$

- b. $1.8 \times 10^{-7} \text{ mol/L}$
- c. $1.5\times 10^{-10}~{\rm mol/L}$
- d. $3.9\times 10^{-13}~{\rm mol/L}$
- e. $4.8\times 10^{40}~{\rm mol/L}$

Explanation: Cu(OH)₂ is a 1:2 salt so $K_{\rm sp} = 4x^3$. Plug in $K_{sp} = 2.2 \times 10^{-20}$, divide by 4 and take the cube root to find that $x = 1.8 \times 10^{-7}$ mol/L. **3.** (Part 1 of 2) Look at the concentration vs time plot to the right for a simple $A \rightarrow B$ reaction scheme. What is the rate of the reaction at 50 seconds?



Explanation: The absolute value of the tangential slope at 50 seconds is 5.8×10^{-4} M/s. A line from (25s,0.04M) to (85s,0.005M) is a good version of the tangential line to use. This is shown below:



4. (Part 2 of 2) In reference to the concentration vs time plot in the previous question, what is the order for this reaction?

- a. third
- b. zero
- •c. first
- d. second
- e. square-root

Explanation: Note the 1/2 life times to go from 0.08 M to 0.04 to 0.02 to 0.01. They are all 30 seconds which means constant half-life which means first order kinetics.

- 5. Kinetic rate laws are determined by:
- a. Analysis of the Arrhenius equation
- •b. Measuring reaction rates while varying the concentration of reactants
 - c. Measuring the equilibrium constant
 - d. Measuring the number of collisions between molecules
- e. Using the coefficients of the balanced chemical reaction

Explanation: Kinetic rate laws are determined by measuring reaction rates at varying concentration of reactants. The coefficients of the balanced chemical reaction do not necessarily indicate the observed kinetics. Measuring the number of collisions between molecules is practically speaking impossible, but if we could, we would still need to know something about the probability of a collision leading to a successful reaction. The equilibrium constant will give us the ratio of rate constants at equilibrium, but we cannot get actual values from this. The Arrhenius equation relates rate constants at various temperatures, but we cannot calculate a rate constant with it alone.

6. Which of the following is false regarding activation energy?

- a. It is independent of temperature
- b. It can be negative
 - c. It determines how fast a reaction will go
 - d. It can be positive
- e. It can be lowered by adding in a catalyst

Explanation: Activation energy can only ever assume a positive value. It can be lowered with the addition of a catalyst, and can get very close to zero with the proper catalyst. Activation energy is usually independent in temperature, cases where it varys with temperature can be ascribed to a change in mechanism. Activation energy directly determines how fast a reaction will go (see Arrhenius equation).

7. The addition of a catalyst to a reaction will speed up the reaction by

- a. catalysts do not speed up reactions.
- b. shifting the equilibrium to favor the products.
- c. shifting the equilibrium to favor the reactants.
- d. making the reaction more exothermic.
- •e. altering the mechanism and lowering the activation energy.
- f. making the reaction more endothermic.
- g. altering the mechanism and raising the activation energy.

Explanation: a catalyst alters the mechanism of a reaction and lowers the barrier of the rate limiting step.

8. Consider the following elementary reaction step that is a part of a kinetic mechanism:

 $C_3H_7I + NH_3 \rightarrow C_3H_7NH_3^+ + I^-$

Classify the step type and give its predicted rate law.

- •a. bimolecular, $rate = k[C_3H_7I][NH_3]$
 - b. termolecular, $rate = k[C_3H_7I][NH_3][C_3H_7NH_3^+]^{-1}[I^-]^{-1}$
 - c. unimolecular, $rate = k[C_3H_7I]$
- d. bimolecular, $rate = k [C_3 H_7 I]^2$
- e. bimolecular, cannot be determined from balanced equation

Explanation: the elementary step involves two molecules so this is a bimolecular step. The rate is predicted to be first order with respect to each molecule.

9. For the reaction

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

The activation energy is 1.0×10^5 J/mol and the value of k at 30°C is 7.3×10^{-5} s⁻¹. What is the value of k at 40°C?

- a. $9.3 \times 10^{-5} \text{ s}^{-1}$
- b. $2.0 \times 10^{-5} \text{ s}^{-1}$
- •c. $2.6 \times 10^{-4} \text{ s}^{-1}$
 - d. $8.4 \times 10^{-13} \ {\rm s}^{-1}$
 - e. $2.0 \times 10^{-6} \text{ s}^{-1}$

Explanation: As temperature increases, the rate constant increases. Use the Arrhenius equation to calculate the new rate constant.

10. Venetian ceruse (PbCO₃) is a white pigment which was used in the 16th century as a cosmetic, often leading to lead poisoning for the user. At a given temperature, the molar solubility of PbCO₃ is 1.9×10^{-6} M, what is the value of K_{sp} ?

- a. 1.9×10^{-6}
- b. 3.6×10^{-12}
- c. 7.4×10^{-14}
- d. 2.7×10^{-17}
- e. 1.5×10^{-13}

Explanation: PbCO₃ is a 1:1 salt so $K_{\rm sp} = x^2 = (1.9 \times 10^{-6})^2 = 3.6 \times 10^{-12}$. Note this is not a "standard" $K_{\rm sp}$ value because it has a higher solubility due to being at a higher temperature.

11. Phosphorus-32 is a radioactive isotope of P that has a half-life of 14.33 days. What mass of P-32 is left after 43 days if you start with a sample containing 200 mg of P-32?

- •a. 25 mg
- b. 12.5 mg
- c. $50~\mathrm{mg}$
- d. 37.5 mg $\,$
- e. 100 mg

Explanation: The half life of a radioactive decay process is the amount of time it takes for half the sample to decay. Radioactive decay is first order and therefore has a constant half live. Because 43 days is exactly 3 half-lives, the initial sample will be cut in half three times which is 1/8. 200/8 = 25 mg.

12. The half-life of U-235 is 700 million years. After 2.8 billion years _____ of the original amount of U-235 remains.

a.
$$\frac{1}{4}$$

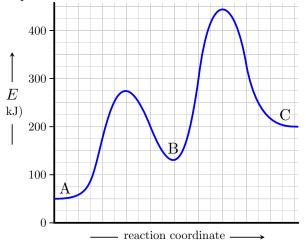
• b. $\frac{1}{16}$

c.
$$\frac{1}{2}$$

- d. $\frac{1}{32}$
- e. $\frac{1}{8}$

Explanation: 2.8 billion years is four half-lives. After the first half-life, one half remains. After the second half-life, half of that, or overall one fourth remains, and so on.

13. The potential energy diagram shown below is for a specific reaction scheme. How many steps are in the reaction mechanism and which step is the rate limiting step?



- a. 3 steps , 1st step limiting
- b. 3 steps , 3rd step limiting
- d. 2 steps , 1st step limiting $% \left({{\left({{{\left({{{\left({{{\left({{{{}}}} \right)}} \right.}$
- e. 3 steps , 2nd step limiting
- f. 2 steps , 2nd step limiting

Explanation: There are 2 maxima and that means 2 steps. The 2nd step (2nd peak) has the largest rise from base to peak (about 315 kJ vs 225 kJ for the first one) and therefore is the rate limiting step.

14. What is the K_{sp} expression for sodium carbonate (Na_2CO_3) ?

•a.
$$K_{sp} = [Na^+]^2 [CO_3^{2-}]$$

b. $K_{sp} = [Na^+]^2 [CO_3^{2-}]^2$
c. $K_{sp} = [Na^+]^2 [C^{4+}] [O^{2-}]^3$
d. $K_{sp} = [Na^+] [CO_3^{2-}]$
e. $K_{sp} = [Na^+] [CO_3^{2-}]^2$

Explanation: Na₂CO₃ is a 2:1 salt, so we need to remember to square the [Na⁺] term. This gives us $K_{sp} = [\text{Na}^+]^2[\text{CO}_3^{2-}].$

15. A reaction with an activation energy of 69 kJ/mol takes 3 hours to reach completion when run at 25°C. At what temperature should this reaction be run in order to drop that time down to only 20 minutes?

- ●a. 51°C
- b. $44^{\circ}\mathrm{C}$
- c. $77^{\circ}C$
- d. $150^{\circ}C$
- e. $37^{\circ}C$

Explanation: Use the Arrhenius equation knowing that the new temperature (T_2) will give a rate constant that is 9 times larger than the one at T_1 . This is because 20 minutes is $1/9^{\text{th}}$ of 3 hours which means $9 \times$ faster. So $k_2/k_1 = 9$.

$$\ln 9 = \frac{69000}{8.314} \left(\frac{1}{298.15} - \frac{1}{T_2} \right)$$

Solving for T_2 gives 323 K which is the same as 51°C.

16. A certain reaction has an activation energy of 252 kJ/mol. As you decrease the temperature the reaction rate will _____ and the activation energy will _____ .

- a. decrease; increase
- •b. decrease; stay the same
- c. increase; decrease
- d. increase; stay the same
- e. increase; increase
- f. decrease; decrease

Explanation: Reaction rates decrease with decreasing temperature because fewer molecules will have enough energy to make it over the activation energy barrier.

17. Solutions of stannous chloride are used in tin electroplating applications. You decide to make a saturated solution of $SnCl_2$ to run some experiments. Which of the following is true?

a.
$$K_{\rm sp} = [{\rm Sn}^{2+}][{\rm Cl}^{-}]$$

b. $K_{\rm sp} = [{\rm Sn}^{2+}]^2 [{\rm Cl}^{-}]$

c.
$$[Sn^{2+}] = [Cl^{-}]$$

- d. $[Sn^{2+}] = 2[Cl^{-}]$
- •e. $[Sn^{2+}] = 0.5[Cl^{-}]$

Explanation: We can start by considering the $K_{\rm sp}$ expressions. We will realize that both choices are incorrect as $K_{\rm sp} = [{\rm Sn}^{2+}][{\rm Cl}^{-}]^2$ for stannous chloride. If we consider the answers about concentration, we will realize that the tin ion concentration has to be half whatever the chloride concentration is, so $[{\rm Sn}^{2+}] = 0.5[{\rm Cl}^{-}]$.

18. The decomposition of azomethane $(C_2H_6N_2)$ follows first order kinetics with a rate constant of 25 min⁻¹. If you start with a concentration of 0.30 M $C_2H_6N_2$, what is the **rate** of the decomposition at a time of exactly 6 seconds into the reaction?

a. $4.0 {\rm M} {\rm min}^{-1}$

- b. $0.10 {\rm M min^{-1}}$
- c. $4.5\times 10^2~{\rm M~min^{-1}}$
- d. $3.7\times10^{-3}~\mathrm{M}~\mathrm{min}^{-1}$
- •e. 0.62 M min^{-1}

Explanation: the rate = $k[C_2H_6N_2]$. The $[C_2H_6N_2]=[C_2H_6N_2]_0 \times e^{-kt}$. $[C_2H_6N_2] = (0.3) \times e^{-2.5}$ = 2.46 ×10⁻² M. The rate = $k[C_2H_6N_2] = (25 \text{ min}^{-1})(2.46 \times 10^{-2} \text{ M}) = 0.62 \text{ M min}^{-1}$ **19**. Consider the following reaction:

 $6 NaOH + Al_2O_3 + 12 HF \implies 2 Na_3AlF_6 + 9 H_2O$

At a given time, water is being produced at a rate of 0.49 M/min for this reaction. What is the corresponding rate for HF during this time?

- a. -0.041 M/min
- b. -0.37 M/min
- c. 0.37 M/min
- •d. -0.65 M/min
- e. $0.65~\mathrm{M/min}$
- f. 0.49 M/min
- g. -0.49 M/min
- h. 0.041 M/min

Explanation: The stoichiometric ratio of HF to H_2O is 12/9. 12/9 times 0.49 is 0.65. HF is a reactant and must be the opposite in sign as the products, therefore the rate of change in HF is -0.65 M/min.

20. CuCl has a $K_{sp} = 1.7 \times 10^{-7}$. In which of the following will it be most soluble?

- a. A 0.25 M solution of NaCl.
- b. Cannot be determined from the information given.
- •c. Pure water.
 - d. A 0.075 M aqueous solution of CuNO₃.
- e. CuCl will have the same solubility in all three of these solutions.

Explanation: The common ion effect will reduce the solubility of CuCl if any Cu^+ or Cl^- are already in solution. Thus, a CuNO₃ or NaCl solution will reduce the solubility of CuCl, making it most soluble in pure water.

21. Consider the possible mechanisms for the following reaction:

$$2NO + O_2 \rightarrow 2NO_2$$

$$\begin{array}{rcl} \mathrm{III} & \mathrm{NO}(\mathrm{g}) \,+\, \mathrm{O}_2(\mathrm{g}) \, \to \, \mathrm{NO}_2(\mathrm{g}) \,+\, \mathrm{O}(\mathrm{g}) & (\mathrm{slow}) \\ & \mathrm{NO}(\mathrm{g}) \,+\, \mathrm{O}(\mathrm{g}) & \to \, \mathrm{NO}_2(\mathrm{g}) & (\mathrm{fast}) \end{array}$$

Given that the empirical rate law for this reaction is found to be $rate = k[NO]^2[O_2]$. Which mechanism(s) is consistant with the rate law?

- a. I and II
- b. I and III

•c. only II

- d. II and III
- e. only III
- f. all three mechanisms are consistant
- g. only I

Explanation: only mechanism II predicts the stated empirical rate law.

22. 17th century processes for the production of felt for use in hats used dilute solutions of mercury nitrate. As a result, mercury poisoning was widespread in hatters of the time, leading to the idiom 'mad as a hatter'. Anyway, what is the net ionic equation for the reaction of aqueous solutions of $Hg(NO_3)_2$ and Na_2S ?

- a. $\mathrm{Hg}^{2+}(\mathrm{aq}) + 2\mathrm{S}^{2-}(\mathrm{aq}) \rightarrow \mathrm{HgS}_{2}(\mathrm{s})$
- b. $Na^+(aq) + NO_3^-(aq) \rightarrow NaNO_3(aq)$
- c. $2Hg^{2+}(aq) + S^{2-}(aq) \rightarrow Hg_2S(s)$

od.
$$\operatorname{Hg}^{2+}(\operatorname{aq}) + \operatorname{S}^{2-}(\operatorname{aq}) \to \operatorname{HgS}(s)$$

e. No reaction occurs because no precipitate is formed.

Explanation: All sodium cation and nitrate anion salts are typically soluble. Additionally, nearly all metal sulfide salts are insoluble. With this information in hand, we can predict that the potential products upon perform a salt metathesis would be sodium nitrate (soluble) and mercury sulfide (insoluble). If we remove all the spectator ions (the ones that remain soluble) we find the net ionic equation: $Hg^{2+}(aq) + S^{2-}(aq) \rightarrow HgS(s)$. 23. The reaction

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

is first order in hydrogen concentration and second order in bromine concentration. What are the units for the rate constant?

a.
$$M^{-1} s^{-1}$$

• b.
$$M^{-2} s^{-1}$$

- c. M $\rm s^{-1}$
- $d. M^{-1}$
- $e. \ s^{-1}$

Explanation: The reaction is third order overall. $rate = k[H_2][Br_2]^2$ In order to get the desired M/s units for rate, k must have units of M⁻² s⁻¹.

24. The reaction $A + B \longrightarrow 2C$ has the rate equation $rate = k[B]^2$. Which is NOT true about this reaction?

- a. The reaction rate will remain constant even if you increase the concentration of reactant A.
- b. Increasing the concentration of reactant B will increase the reaction rate.
- •c. The mechanism for this reaction could have only a single-step.
 - d. Increasing the temperature would increase the reaction rate.

Explanation: The reaction is zeroth order in A and second order in B, so the concentration of B will affect the rate of reaction but the concentration of A will not. If this reaction was an elementary, one-step reaction, the rate law would have to be rate = k[A][B].

25. Rank the following salts in terms of their molar solubilities from smallest to largest:

$$\begin{split} &\text{Be(OH)}_2 \ K_{sp} = 6.9 \times 10^{-22} \\ &\text{CaF}_2 \ K_{sp} = 3.5 \times 10^{-11} \\ &\text{Fe(OH)}_3 \ K_{sp} = 2.8 \times 10^{-39} \\ &\text{CuBr} \ K_{sp} = 6.3 \times 10^{-9} \\ &\text{a. Be(OH)}_2 < \text{Fe(OH)}_3 < \text{CuBr} < \text{CaF}_2 \end{split}$$

b. $Fe(OH)_3 < Be(OH)_2 < CaF_2 < CuBr$

•c. $Fe(OH)_3 < Be(OH)_2 < CuBr < CaF_2$

- d. $Be(OH)_2 < Fe(OH)_3 < CaF_2 < CuBr$
- e. $CuBr < Be(OH)_2 < Fe(OH)_3 < CaF_2$

Explanation: We are ranking the salts by their molar solubility, NOT their $K_{\rm sp}$'s. Solve for the molar solubility for each salt by applying the correct $K_{\rm sp}$ relationship. After doing this, the correct ranking is found to be: Fe(OH)₃ < Be(OH)₂ < CuBr < CaF₂.

After you are finished and have all your answers circled, go to the front of the room and then use the QR code show below to pull up the virtual answer page for your exam. Enter the appropriate info plus all your answers - click the SUBMIT button. Double check your choices on the next page. Once your are sure, click the submit button on that page to enter your answers. Make sure you get the confirmation screen (different background color!) and show it to the TA or proctor. After that, turn in your exam and scratch paper. You're free to leave after that.



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