$\boxed{\text{Solution}}$

CHEM 104
PLI 29 Mock Exam
Tuesday, July 12, 2016

Mock Exam I

1. Interferon is a water-soluble, non-dissociating protein. A 2.50 mL solution prepared by dissolving 15.0 mg of interferon in water exhibits an osmotic pressure of 5.80 mm Hg at 25 °C. What is the molar mass of interferon?

$$\pi = cRT \longrightarrow c = \frac{\pi}{RT}$$

$$\pi = 5.80\text{ mmHg}\left(\frac{1\text{ atm}}{760\text{ mmHg}}\right) = 7.632\times10^{-3}\text{ atm} \qquad T = 25+273 = 298\text{K}$$

$$c = \frac{\pi}{RT} = \frac{7.632\times10^{-3}\text{ atm}}{0.08206\frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}(298\text{K})} = 3.121\times10^{-4}\frac{\text{mol}}{\text{L}}$$

$$0.00250\text{L}\left(3.121\times10^{-4}\frac{\text{mol}}{\text{L}}\right) = 7.802\times10^{-7}\text{ mol} \rightarrow \frac{0.015\text{g}}{7.802\times10^{-7}\text{mol}} = \boxed{1.92\times10^{4}\text{ g/mol}}$$

2. Assuming complete dissociation, which 0.10 *m* electrolyte solution will show the largest freezing point depression?

(A) HCl $i=2$
(B) $NaNH_4$ $i=2$
(C) $CaBr_2$ $i=3$
(D) $MgSO_4$ $i=2$
[✓ (E) K_3PO_4] $i=4$

3. The half-life of a first-order reaction is 1.5 hours. How much time is needed for 94% of the reactant to change to product?

↓ 6.0% remaining

① find k: $\ln\frac{1}{2} = -kt$

$$k = -\frac{\ln\frac{1}{2}}{t} = -\frac{\ln\frac{1}{2}}{1.5\text{ hrs}} = 0.4621\text{ hr}^{-1}$$

② find $t_{0.6}$: $t_{0.6} = -\frac{\ln\frac{1}{2}}{0.4621\frac{1}{\text{hr}}} = \boxed{6.1\text{ hrs}}$

4. When the kinetics of the reaction, 2A + 2B → C were studied using the method of initial rates, the data in the table below were obtained.

Trial	$[A]_0$ (M)	$[B]_0$ (M)	Initial Rate of Formation of C (M/s)
1	$\times\frac{1}{2}$ 0.060	$\times 3$ 0.040 $\times 2$	3.6×10^{-4} $\times 2$
2	0.060	0.080	$\times 1.5$ 7.2×10^{-4}
3	0.030	0.120	5.4×10^{-4}

What is the rate law for the reaction?

first order in [B], first order in [A]

$\boxed{\text{rate} = K[A][B]}$

5. For the reaction $5O_{2(g)} + 4NH_{3(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$, if NH_3 is being consumed at a rate of 0.50 M/s, at what rate is H_2O being formed?

$$-\frac{1}{4}\left(\frac{\Delta[NH_3]}{\Delta t}\right) = \frac{1}{6}\left(\frac{\Delta[H_2O]}{\Delta t}\right)$$

$$\frac{\Delta[H_2O]}{\Delta t} = -\frac{6}{4}\left(\frac{\Delta[NH_3]}{\Delta t}\right) = -\frac{6}{4}\left(-0.50\ \frac{M}{s}\right) = \boxed{0.75\ \frac{M}{s}}$$

6. A solution of 5.00 g of which ionic solid, in 1 L of solution at 25 °C, has the largest osmotic pressure? $\pi = CiRT \rightarrow RT$ is same for all; look at Ci.

(A) $CaBr_2$ (molar mass = 199.9 g/mol) 0.015
(B) RbF (molar mass = 104.5 g/mol) 0.019
(C) $AlBr_3$ (molar mass = 266.7 g/mol) 0.015
[✓ (D)] KNO_3 (molar mass = 101.1 g/mol) 0.020
(E) NaI (molar mass = 149.9 g/mol) 0.013

$$Ci = \frac{mol}{L}i = \frac{\left(\frac{5.0g}{\text{molar mass}}\right)}{L} \cdot i$$

find the largest $\frac{i}{\text{molar mass}}$

7. A substance XY decomposes in a second-order reaction. A solution that is initially 1.00 M in XY requires 0.50 hours for its concentration to decrease to 0.50 M. How much time will it take for a solution of XY to decrease in concentration from 2.00 M to 0.25 M?

$$\frac{1}{[XY]_t} = Kt + \frac{1}{[XY]_0} \rightarrow K = \frac{\frac{1}{[XY]_t} - \frac{1}{[XY]_0}}{t} = \frac{\frac{1}{0.50M} - \frac{1}{1.00M}}{0.50\text{ hrs}} = 2\ \frac{1}{M\cdot hr}$$

$$\downarrow$$

$$t = \frac{\frac{1}{[XY]_t} - \frac{1}{[XY]_0}}{K} = \frac{\frac{1}{0.25M} - \frac{1}{2.00M}}{2\ \frac{1}{M\cdot hr}} = \boxed{1.75\text{ hours}}$$

Passage II (Questions 8–14)

A chemist interested in the reactivity of iodine concentrated his study on two reactions: the decomposition of gaseous hydrogen iodide (Reaction 1) and the reaction between iodide ions and persulfate ions (Reaction 2).

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

Reaction 1

$$3I^-(aq) + S_2O_8^{2-}(aq) \rightleftharpoons I_3^-(aq) + 2SO_4^{2-}(aq)$$

Reaction 2

The value of the rate constant for Reaction 1 was studied as a function of temperature. The results are shown below.

Table 1

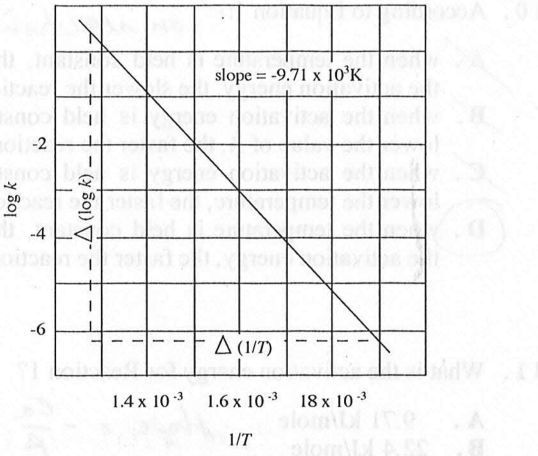
T(K)	$1/T$ (K^{-1})	k (l•mol^{-1}sec^{-1})	log k
555	1.80×10^{-3}	3.52×10^{-7}	–6.453
575	1.74×10^{-3}	1.22×10^{-6}	–5.913
645	1.55×10^{-3}	8.59×10^{-5}	–4.066
700	1.43×10^{-3}	1.16×10^{-3}	–2.936
781	1.28×10^{-3}	3.95×10^{-2}	–1.403

For any reaction, the activation energy (E_a) is related to the rate constant (k) by the Arrhenius equation (Equation 1):

$$k = A \times 10^{(-Ea\,/\,2.303RT)}$$

Equation 1

where R = 8.314 J mol^{-1}K^{-1}, T is the temperature in Kelvin, and A is a constant, called the frequency factor. Figure 1 shows a graph of log k vs. $1/T$ for Reaction 1.



In order to determine the initial rate of Reaction 2, the following data were collected:

Table 2

Experiment	[I$^-$] (M)	[S$_2$O$_8$$^{-2}$] ($M$)	Initial rate of reaction (M / sec)
1	0.21	×2 0.15	×2 1.14
2	0.21 ×2	0.30	2.28 ×2
3	0.42	0.15	2.28

8. What is the rate law for Reaction 2?

A. Rate = $k[I^-]^2[S_2O_8^{2-}]$

B. Rate = $k[S_2O_8^{2-}]$

[✓ **C.**] Rate = $k[I^-][S_2O_8^{2-}]$

D. Rate = $k[I^-][S_2O_8^{2-}]^2$

first order in $[I^-]$ and in $[S_2O_8^{-2}]$

9. What is the numerical value of the rate constant for Reaction 2?

A. 7.6 mol/L•sec

[✓ **B.**] 36 mol/L•sec

C. 172 mol/L•sec

D. 241 mol/L•sec

$$K = \frac{rate}{[I^-][S_2O_8^{2-}]} = \frac{1.14\ M/s}{0.21M\,(0.15M)}$$

estimate and approximate!

$$\lesssim \frac{1.14}{0.03} \rightarrow \lesssim 38\ M/s$$

you don't even need the Arrhenius equation if you understand the effects of activation energy and temperature on reaction rate.

10. According to Equation 1:

A. when the temperature is held constant, the lower the activation energy, the slower the reaction.
B. when the activation energy is held constant, the lower the value of *A*, the faster the reaction.
C. when the activation energy is held constant, the lower the temperature, the faster the reaction.
[✓ D.] when the temperature is held constant, the lower the activation energy, the faster the reaction.

11. What is the activation energy for Reaction 1?

A. 9.71 kJ/mole
B. 22.4 kJ/mole
C. 80.7 kJ/mole
[✓ D.] 186 kJ/mole

$$\text{slope} = -\frac{E_a}{R} = -9710\text{ K}$$

$$E_a = 9710\text{K}(2.303)\left(0.008314\frac{\text{kJ}}{\text{mol}\cdot\text{K}}\right)$$

$$\sim 9700(0.020) = 194\text{ kJ/mol}$$

12. In Figure 1, what does the intercept with the *y*-axis represent?

[✓ A.] log *A*
B. log *k*
C. $-E_a$
D. $-\frac{1}{RT}$

$$\log k = \frac{-E_a}{2.303R}\left(\frac{1}{T}\right) + \log A$$

13. If the rate of disappearance of I^- in Reaction 2 is 2.5×10^{-3} mol/(L•s), what is the rate of formation of SO_4^{2-}?

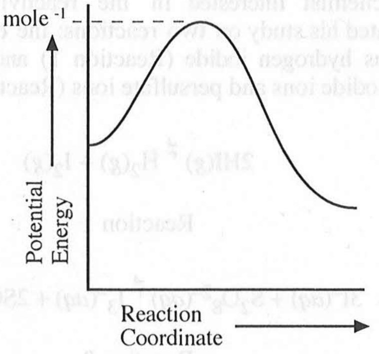
[✓ A.] 1.7×10^{-3} mol/(L•s)
B. 3.8×10^{-3} mol/(L•s)
C. 5.0×10^{-3} mol/(L•s)
D. 8.3×10^{-4} mol/(L•s)

$$-\frac{1}{3}\left(\frac{\Delta[I^-]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta[SO_4^{2-}]}{\Delta t}\right)$$

$$\frac{\Delta[SO_4^{2-}]}{\Delta t} = -\frac{2}{3}\left(\frac{\Delta[I^-]}{\Delta t}\right) = \underbrace{-\frac{2}{3}\left(-2.5\times10^{-3}\ \text{M/s}\right)}_{} = \frac{5}{3}\times10^{-3}\ \frac{\text{M}}{\text{s}} \sim 1.7\ \frac{\text{M}}{\text{s}}$$

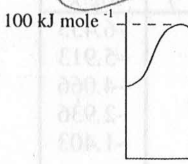
or, just see that the answer must be slightly less than 2.5×10^{-3} M/s, since we are taking a fraction. Therefore, choice A is our only option.

14. The reaction profile shown below is for an uncatalyzed reaction.

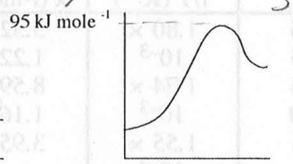


Which of the following is the reaction profile for the same reaction after the addition of a catalyst?

[✓ A.]

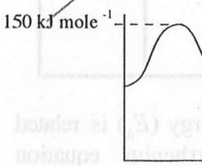


C.

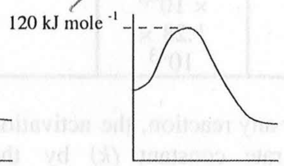


lower Ea, same overall ΔH

B.



D.



15. A reaction has a rate constant *k* = 8.54 x 10^{-4} $M^{-1}s^{-1}$ at 45 ºC, and an activation energy E_a = 90.8 kJ. What is the value of *k* at 25 ºC?

$$\ln\frac{K_2}{K_1} = \frac{-E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\ln K_2 = -\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) + \ln K_1$$

$$= -\frac{90.8\,KJ}{0.008314\,\frac{KJ}{mol\,K}}\left(\frac{1}{298\,K}-\frac{1}{318\,K}\right) + \ln(8.54\times10^{-4}\,\tfrac{1}{M\cdot s}) = -9.37$$

$$e^{\ln K_2} = e^{-9.37}$$

$$K_2 = e^{-9.37} = \boxed{8.52\times10^{-5}\,\frac{1}{M\cdot s}}$$

16. What is the mole fraction of CH_3OH in an aqueous solution that is 12.0 *m* in CH_3OH?

$$12.0\,m = \frac{12.0\,mol\;CH_3OH}{1\,kg\;H_2O}$$

$$\frac{1000\,g\;H_2O}{1\,Kg\;H_2O}\left(\frac{1\,mol}{18\,g}\right) = \frac{55.5\,mol\;H_2O}{1\,Kg\;H_2O}$$

$$\frac{12.0\,mol\;CH_3OH}{55.5 + 12.0\;mol\;total} = \boxed{0.178}$$

17. For the reaction, 2A + B → C + D, the rate law is: Rate = *k*[B].

Which of the following mechanisms is consistent with this information?

~~(A)~~ A + B → M (slow) rate = k[A][B]
A + M → C + D (fast)

~~(B)~~ A + A → M (fast) rate = k[B] but overall reaction is
B → C + D (slow) 2A + B → C + D + M

(C) B → $\cancel{M}$ (slow) rate = k[B] and overall reaction is
A + $\cancel{M}$ → $\cancel{N}$ (fast) 2A + B → C + D ✓
$\cancel{N}$ + A → C + D (fast)

~~(D)~~ B → M (fast)
A + M → N (slow) rate = k[A][M]
N + A → C + D (fast)

~~(E)~~ A + A→ M (slow) rate = k[A]^2
M + B → C + D (fast)

18. Which of the following decreases with increasing intermolecular forces?

- (A) Boiling point
- (B) Molar enthalpy of vaporization ($\Delta_{vap}H^o$)
- [✓ (C)] Vapor pressure
- (D) Viscosity
- (E) Surface tension

19. The Henry's Law constant for oxygen gas in water at 25 °C $k_{O_2} = 1.3 \times 10^{-3}$ M/atm. What is the partial pressure of O_2 above a solution at 25 °C with an O_2 concentration of 2.3×10^{-4} M at equilibrium?

$$S_g = K_H \cdot P_g$$

$$P_g = \frac{S_g}{K_H} = \frac{2.3 \times 10^{-4}\ M}{1.3 \times 10^{-3}\ \frac{M}{atm}} = \boxed{0.18\ atm}$$

20. Which mixture of water and H_2SO_4 represents a solution with a concentration that is closest to 30% by mass H_2SO_4? 98.08g/mol

- (A) 30 g H_2SO_4 + 100 g H_2O ← don't fall for this one! $\frac{30}{130} \neq 0.30$
- [✓ (B)] 1 mol H_2SO_4 + 200 g H_2O ~ $100/300 = 0.30$
- (C) 30 mol H_2SO_4 + 0.70 kg H_2O
- (D) 0.30 mol H_2SO_4 + 0.70 mol H_2O
- (E) 0.30 mol H_2SO_4 + 100 mol H_2O

21. The vapor pressure of water at 31 °C is 33.7 mmHg. When you dissolve 931.0 g of acetone (CH_3COCH_3) in 32.50 kg of water, what is the vapor pressure of water over the solution at 31 °C?

$$P_{solution} = P_{solvent} \cdot X_{solvent}$$

$$931.0g\ acetone \left(\frac{1mol}{58.08g}\right) = 16.0\ mol\ acetone$$

$$32500g\ H_2O \left(\frac{1mol}{18g}\right) = 1803.6\ mol\ H_2O$$

$$X_{solvent} = \frac{1803.6\ mol\ H_2O}{1803.6 + 16\ mol\ total}$$

$$= 0.9912$$

$$= 33.7 mmHg (0.9912)$$

$$= \boxed{33.4\ mmHg}$$

22. The data below were collected for this reaction at 500 °C: CH3CN (g) → CH3NC (g)

Time (hr)	[CH₃CN] (M)	$\ln[CH_3CN]$	$1/[CH_3CN]$
0.0	1.000	0	1
5.0	0.794	−0.231	1.259
10.0	0.631	−0.460	1.585
15.0	0.501	−0.691	1.996
20.0	0.393	−0.934	2.544
25.0	0.316	−1.152	3.165

a) What is the order of the reaction? Please briefly explain your reasoning.

This reaction is <u>first order</u> because as time increases in constant increments, so too does the value for $\ln[CH_3CN]$. A graph of $\ln[CH_3CN]$ vs. time would be approximately linear.

b) What is the value of the rate constant at this temperature?

$$\ln[A]_t = -kt + \ln[A]_0$$

$$k = \frac{\ln[A]_t - \ln[A]_0}{-t} = \frac{-0.231 - 0}{-5} = \boxed{0.046\ \frac{1}{hr}}$$

c) What is the half-life for this reaction (at the initial concentration)?

$$\ln\tfrac{1}{2} = -kt + \ln 1$$

$$t = \frac{\ln\frac{1}{2}}{-k} = \frac{\ln\frac{1}{2}}{0.046\frac{1}{hr}} = \boxed{15.1\ hrs}$$

d) How long will it take for 90% of the CH3CN to convert to CH3NC?

$$\ln 0.1 = -kt + \ln 1$$

$$t = \frac{\ln 0.1}{0.046} = \boxed{50.0\ hrs}$$

$\nearrow CaCl_2$

23. During the winter, much of the salt you see melting ice is calcium chloride, which has a solubility of 74.5 g per 100.0g of cold water. What is the lowest temperature ice that calcium chloride salt can melt assuming complete dissociation?

$\Delta T_{fp} = K_{fp}\, m\, i \qquad K_{fp} = -1.86\,°C/m$

$i = 3$

$m = \frac{74.5\,g}{100\,g\ H_2O}\left(\frac{1\,mol}{110.98\,g}\right) = \frac{0.671\,mol}{0.100\,kg} = 6.71\,m$

$\Delta T_{fp} = -1.86\,\frac{°C}{\cancel{m}}\,(6.71\,\cancel{m})\,(3)$

$= -37.4°C$

The melting point of water is 0°C, so the lowest temperature of ice that $CaCl_2$ can melt is $\boxed{-37.4°C}$.

24. The data shown below were collected for the second-order reaction:

$Cl_2\,(g) + 2\,H_2\,(g) \rightarrow 2\,HCl\,(g) + H_2\,(g)$

Temp. (K)	Rate Constant ($M^{-1}\,s^{-1}$)
90	0.00357
100	0.0773
110	0.956

Please determine the activation energy and frequency factor for the reaction.

$$\ln\frac{K_2}{K_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a = \frac{-R\ln\frac{K_2}{K_1}}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = \frac{-8.314\,\frac{J}{mol\cdot K}\left(\ln\frac{0.0773}{0.00357}\right)}{\left(\frac{1}{100K} - \frac{1}{90K}\right)} = 2.3\times10^4\ J/mol$$

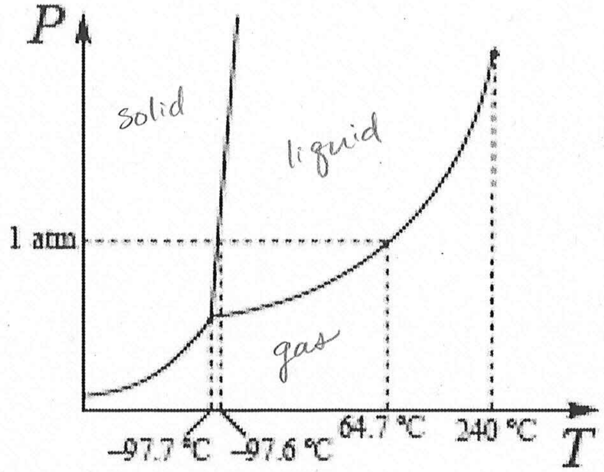
or $\boxed{23\ kJ/mol}$

$$K = Ae^{-E_a/RT}$$

$$A = \frac{K}{e^{-E_a/RT}} = \frac{0.00357\,\frac{1}{M\cdot s}}{\left(e^{\frac{-23\,kJ/mol}{(0.008314\,\frac{kJ}{mol\cdot K})(90K)}}\right)} = \boxed{8.0\times10^{10}\ \frac{1}{s}}$$

← units should match those of the rate constant for whatever order rxn is.

25. Below is the phase diagram of methanol:



a) True or False:

i. T Solid methanol is denser than liquid methanol.

ii. F Solid methanol sublimes at atmospheric pressure.

iii. T Solid, liquid, and gaseous methanol cannot coexist at atmospheric pressure.

iv. F It is possible to have liquid methanol at −100 °C.

v. T It is possible to have gaseous methanol at 1 atm.

b) What is the boiling point of methanol at atmospheric pressure? 64.7°C

c) What is the freezing point of methanol at atmospheric pressure? −97.6°C