Carleton UNIVERSITY

CHEM 1006 A
Winter 2018

Midterm #2: Deferred

Test duration: 80 minutes
Instructor: Alyssa Nause

Student Name: Solutions

Student Number: ______________________

Answer the questions on the exam paper.

If more space is needed, use reverse of exam pages.

Part A: Short Answer (5 marks each)

5

1. Each of the compounds below are amphiprotic. Indicate the likely conjugate acid and likely conjugate base of each compound:
   a. H_2O
   b. NH_3

a) H_2O as acid: OH^- is conjugate base (1.25)
H_2O as base: H_3O^+ is conjugate acid (1.25)

b) NH_3 as acid: NH_2^- is conjugate base (1.25)
NH_3 as base: NH_4^+ is conjugate acid (1.25)

5

2. a) Define the relation between the rate of a reaction and the temperature of the reaction.
   b) Describe what impact temperature has on the activation energy of the reaction and the progress of the reaction.

a) Rate of reaction $\propto$ Temperature
(increasing the temperature usually increases the rate of reaction; they are proportional)
(2.5)

b) Temperature has no impact on activation energy. (1)

The rate increase with increased temperature will allow the reaction to progress more quickly.
(1.5)

/5

3. The following overall reaction has part of a potential mechanism listed below. Predict the missing step of the mechanism.

   Overall: $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$

   Mechanism:

   1) $Cl_{2(g)} \rightleftharpoons 2Cl_{(g)}$

   2) Unknown

   3) $H_{(g)} + Cl_{(g)} \rightarrow HCl_{(g)}$

So far mechanism gives:

$Cl_{2(g)} + H_{(g)} \rightarrow Cl_{(g)} + HCl_{(g)}$

overall: $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$

(missing/extra circled)

Proposed Step 2: $Cl_{(g)} + H_{2(g)} \rightarrow HCl_{(g)} + H_{(g)}$

1 present, 1 present, 1 present, 1 present

0.5 phases

0.5 correct order / placement

/5

4. Some acids, like H_2SO_4 (sulfuric acid) can lose more than one proton in an acid-base reaction. Identify the conjugate acid-base pairs of each of the reactions below:

   a. $H_2SO_{4\,(aq)} + H_2O_{(l)} \rightarrow HSO_4^-{}_{(aq)} + H_3O^+{}_{(aq)}$

   b. $HSO_4^-{}_{(aq)} + H_2O_{(l)} \rightarrow SO_4^{2-}{}_{(aq)} + H_3O^+{}_{(aq)}$

a) $H_2SO_{4(aq)} + H_2O_{(l)} \rightarrow HSO_4^-{}_{(aq)} + H_3O^+{}_{(aq)}$

Acid (1.25) → C.B. ; Base (1.25) → C.A.

b) $HSO_4^-{}_{(aq)} + H_2O_{(l)} \rightarrow SO_4^{2-}{}_{(aq)} + H_3O^+{}_{(aq)}$

Acid (1.25) → C.B. ; Base (1.25) → C.A.

Part B: Long Answer Problems (10 marks each)

/10

5. One of the industrial methods used to form concentrated sulfuric acid ($H_2SO_{4(l)}$) is the "Contact Process" which utilizes vanadium oxide (V_2O_5) as a catalyst. The major steps of this process are shown below. The overall reaction has an energy change of –212 kJ/mol.

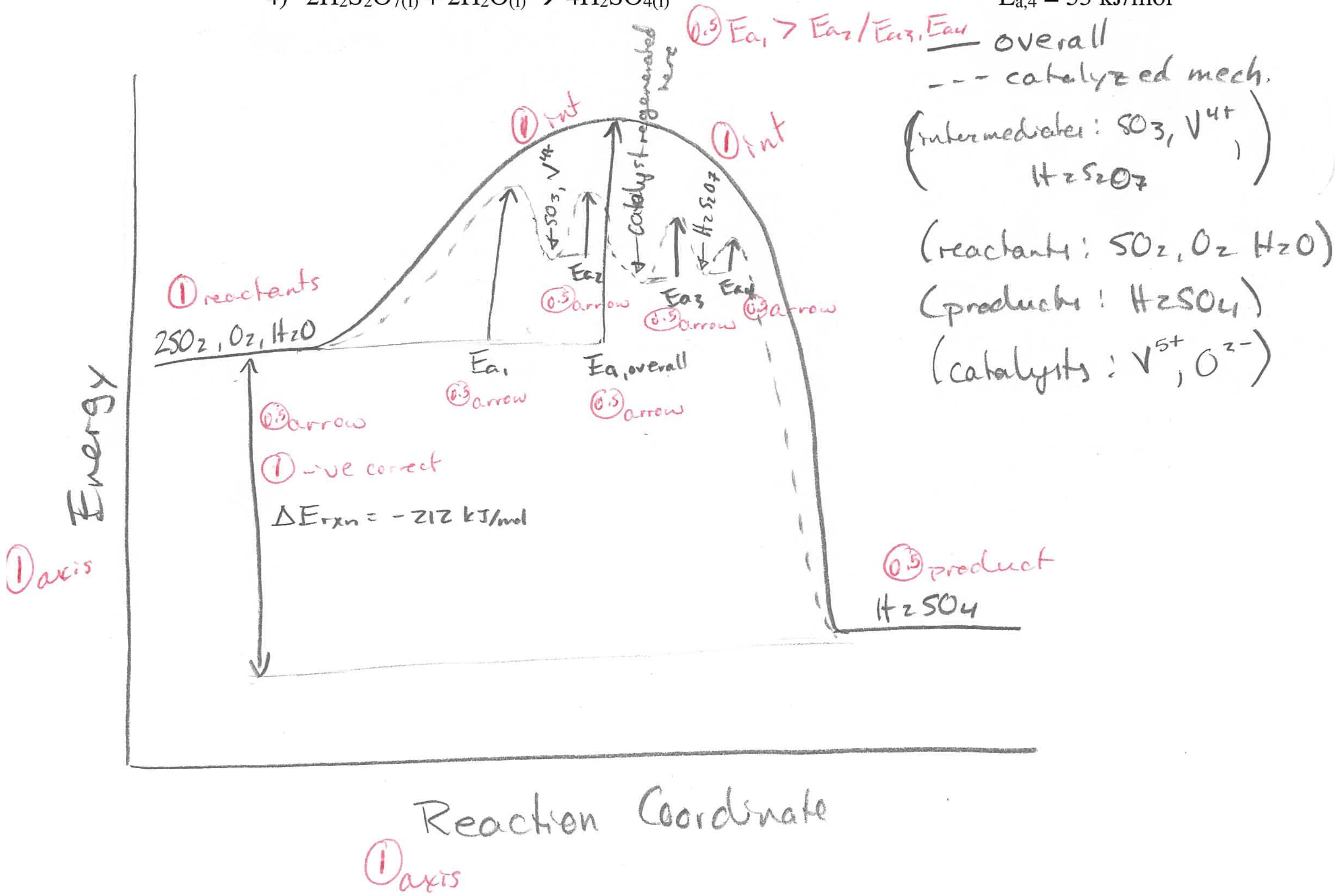
   a. Sketch an energy profile for the overall reaction and its catalyzed mechanism (sketch both on the same plot).
   b. On your sketched energy profile, include arrows to indicate each activation energy and the energy change of the reaction.
   c. Note each non-catalyst species in the catalyzed mechanism in its appropriate location on the energy profile.

Overall: $E_{a,overall}$ = 315 kJ/mol

$$2SO_{2(g)} + O_{2(g)} + H_2O_{(l)} \xrightarrow{V_2O_{5(s)} \rightarrow 2V^{5+}{}_{(aq)} + 5O^{2-}{}_{(aq)}} 2H_2SO_{4(l)}$$

Catalyzed Mechanism:

1) $2SO_{2(g)} + 4V^{5+}{}_{(aq)} + 2O^{2-}{}_{(aq)} \rightarrow 2SO_{3(g)} + 4V^{4+}{}_{(aq)}$ $\quad E_{a,1}$ = 95 kJ/mol
2) $4V^{4+}{}_{(aq)} + O_{2(g)} \rightarrow 4V^{5+}{}_{(aq)} + 2O^{2-}{}_{(aq)}$ $\quad E_{a,2}$ = 44 kJ/mol
3) $2H_2SO_{4(l)} + 2SO_{3(g)} \rightarrow 2H_2S_2O_{7(l)}$ $\quad E_{a,3}$ = 65 kJ/mol
4) $2H_2S_2O_{7(l)} + 2H_2O_{(l)} \rightarrow 4H_2SO_{4(l)}$ $\quad E_{a,4}$ = 53 kJ/mol



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6. For the following reaction and experimental data:
   a. Determine the activation energy.
   b. Determine the rate constant at 100.0°C, and comment on the effect this lower temperature has on the reaction progress.

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

	Experimental rate constant ($M^{-1}\ s^{-1}$)	Temperature (°C)
Trial 1	6.67×10^{-8}	673
Trial 2	2.70×10^{-5}	452

a) $\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{E_a}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ (0.5) equation

convert

$T_1 = 673°C = 946.15 K$ (0.5)

$T_2 = 452°C = 725.15 K$ (0.5)

$R = 8.314\ J/k\ mol$

$$\ln\left(\frac{2.70 \times 10^{-5}\ M^{-1}s^{-1}}{6.67 \times 10^{-8}\ M^{-1}s^{-1}}\right) = \frac{E_a}{8.314 J/k mol}\left(\frac{1}{946.15K} - \frac{1}{725.15K}\right)$$

(1) 1 vs 2 correct

$$6.003387 = \frac{E_a}{8.314 J/k mol}\left(-0.00032211\ K^{-1}\right)$$

$E_a = -154953.698\ J/mol$

$E_a = -1.55 \times 10^5\ J/mol$ (1) calc (no errors) (1) result

(or $E_a = -1.55 \times 10^2\ kJ/mol$) (0.5) sig. fig.

b) $k_1 = 6.67 \times 10^{-8}\ M^{-1}s^{-1}$, $T_1 = 946.15K$

$k_2 = ?$, $T_2 = 100.0°C = 373.15K$ (0.5) convert

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

(cont'd on page 8)

(6. b))

$$\ln\left(\frac{k_2}{6.67\times10^{-8}\ M^{-1}s^{-1}}\right) = \frac{-154953.698\ J/mol}{8.314\ J/K\ mol}\left(\frac{1}{946.15K} - \frac{1}{373.15K}\right)$$

(1) 1 vs 2 correct

$$\ln\left(\frac{k_2}{6.67\times10^{-8}\ M^{-1}s^{-1}}\right) = 30.2484$$

$$\ln(k_2) - \ln(6.67\times10^{-8}\ M^{-1}s^{-1}) = 30.2484$$

$$\ln(k_2) = 13.72539$$

$$k_2 = e^{13.72539}$$

(1) calc (no errors)

$$k_2 = 913819.06\ M^{-1}s^{-1}$$

(1) result

$$k_2 = 9.14\times10^{5}\ M^{-1}s^{-1}$$

(0.5) sig. figs.

This lower temperature lets the reaction progress Faster (unusual, but not impossible).

(1) impact of low temp

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7. Determine the rate law for the following given mechanism. If possible, substitute any invalid compounds in the predicted rate law to determine the corrected predicted rate law.

Overall: $NH_4^+{}_{(aq)} + HNO_{2\,(aq)} \longrightarrow N_{2(g)} + 2H_2O_{(l)} + H^+{}_{(aq)}$

Mechanism:

1) $HNO_{2\,(aq)} + H^+{}_{(aq)} \rightleftharpoons H_2O_{(l)} + NO^+{}_{(aq)}$ (fast, reversible)

2) $NH_4^+{}_{(aq)} \rightleftharpoons NH_{3(aq)} + H^+{}_{(aq)}$ (fast, reversible)

3) $NO^+{}_{(aq)} + NH_{3(aq)} \rightarrow NH_3NO^+{}_{(aq)}$ (slow)

3) $NH_3NO^+{}_{(aq)} \rightarrow H_2O_{(l)} + H^+{}_{(aq)} + N_{2(g)}$ (fast)

(1) predicted

Predicted Rate law: $\text{Rate} = k_3[NO^+{}_{(aq)}][NH_{3(aq)}]$

both $[NO^+]$ and $[NH_3]$ are intermediate

(2) both int.

Replace $[NO^+{}_{(aq)}]$ with Equality of rates of reaction (1):

(0.5) use (1)

Rate (1) Forward = Rate (1) backward

$$k_1[HNO_{2\,(aq)}][H^+{}_{(aq)}] = k_{-1}[H_2O_{(l)}][NO^+{}_{(aq)}]$$

$$[NO^+{}_{(aq)}] = \frac{k_1[HNO_{2\,(aq)}][H^+{}_{(aq)}]}{k_{-1}[H_2O_{(l)}]}$$

(1) rearrange

Replace $[NH_{3\,(aq)}]$ with Equality of Rates of reaction (2):

(0.5) use (2) Rate (2) Forward = Rate (2) backward

$$k_2[NH_4^+{}_{(aq)}] = k_{-2}[NH_{3\,(aq)}][H^+{}_{(aq)}]$$

$$[NH_{3\,(aq)}] = \frac{k_2[NH_4^+{}_{(aq)}]}{k_{-2}[H^+{}_{(aq)}]}$$

(1) rearrange

(cont'd on page 10)

(7.)

$$Rate = k_3 [NO^+_{(aq)}][NH_{3\,(aq)}]$$

$$Rate = k_3 \left(\frac{k_1}{k_{-1}}\right)\left(\frac{[HNO_{2(aq)}][H^+_{(aq)}]}{[H_2O_{(l)}]}\right)\left(\frac{k_2}{k_{-2}}\right)\left(\frac{[NH_4^+{}_{(aq)}]}{[H^+_{(aq)}]}\right)$$

(1) sub. both

$$Rate = \frac{k_3 k_1 k_2}{k_{-1} k_{-2}} \frac{[HNO_{2(aq)}]\cancel{[H^+_{(aq)}]}[NH_4^+{}_{(aq)}]}{[H_2O_{(l)}]\cancel{[H^+_{(aq)}]}}$$

$$Rate = \frac{k_3 k_1 k_2}{k_{-1} k_{-2}} \frac{[HNO_{2(aq)}][NH_4^+{}_{(aq)}]}{[H_2O_{(l)}]}$$

(1) simplify

(1) final rate law

(1) all k's accounted for

(OR! $Rate = k [HNO_{2(aq)}][NH_4^+{}_{(aq)}][H_2O_{(l)}]^{-1}$,

where $k = \frac{k_3 k_1 k_2}{k_{-1} k_{-2}}$)

Equations and Constants:

$R = 8.314\ J\ K^{-1}\ mol^{-1}$

$N_{Av} = 6.022x10^{23}\ mol^{-1}$

$n = m/M$

$c = n/V$

$\rho = m/V$

$b = n/m$

$X_C = n_C/n_{total}$

$t_{1/2} = \ln 2\ /\ ak$

$t_{1/2} = 1\ /\ 2k[A]_o$

$\ln[A] = -akt + \ln[A]_o$

$1/[A] = 2kt + 1/[A]_o$

$Rate = k[A]^x[B]^y$

$k_1[A_2] = k_{-1}[A]^2$

$k = Ae^{-Ea/RT}$

$\ln(k) = \ln(A) - E_a/RT$

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

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$0 = ax^2 + bx + c$

$1\ atm = 1.01325x10^5\ Pa = 760\ Torr = 1.01325\ bar$

$T(K) = T(^oC) + 273.15$

Key:

Element Name Atomic number **Symbol** Atomic weight (mean relative mass)

1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Hydrogen 1 **H** 1.008																		Helium 2 **He** 4.0026
Lithium 3 **Li** 6.94	Beryllium 4 **Be** 9.0122												Boron 5 **B** 10.81	Carbon 6 **C** 12.011	Nitrogen 7 **N** 14.007	Oxygen 8 **O** 15.999	Fluorine 9 **F** 18.998	Neon 10 **Ne** 20.180
Sodium 11 **Na** 22.990	Magnesium 12 **Mg** 24.305												Aluminium 13 **Al** 26.982	Silicon 14 **Si** 28.085	Phosphorus 15 **P** 30.974	Sulfur 16 **S** 32.06	Chlorine 17 **Cl** 35.45	Argon 18 **Ar** 39.948
Potassium 19 **K** 39.098	Calcium 20 **Ca** 40.078(4)		Scandium 21 **Sc** 44.956	Titanium 22 **Ti** 47.867	Vanadium 23 **V** 50.942	Chromium 24 **Cr** 51.996	Manganese 25 **Mn** 54.938	Iron 26 **Fe** 55.845(2)	Cobalt 27 **Co** 58.933	Nickel 28 **Ni** 58.693	Copper 29 **Cu** 63.546(3)	Zinc 30 **Zn** 65.38(2)	Gallium 31 **Ga** 69.723	Germanium 32 **Ge** 72.63	Arsenic 33 **As** 74.922	Selenium 34 **Se** 78.96(3)	Bromine 35 **Br** 79.904	Krypton 36 **Kr** 83.798(2)
Rubidium 37 **Rb** 85.468	Strontium 38 **Sr** 87.62		Yttrium 39 **Y** 88.906	Zirconium 40 **Zr** 91.224(2)	Niobium 41 **Nb** 92.906(2)	Molybdenum 42 **Mo** 95.96(2)	Technetium 43 **Tc** [97.91]	Ruthenium 44 **Ru** 101.07(2)	Rhodium 45 **Rh** 102.91	Palladium 46 **Pd** 106.42	Silver 47 **Ag** 107.87	Cadmium 48 **Cd** 112.41	Indium 49 **In** 114.82	Tin 50 **Sn** 118.71	Antimony 51 **Sb** 121.76	Tellurium 52 **Te** 127.60(3)	Iodine 53 **I** 126.90	Xenon 54 **Xe** 131.29
Caesium 55 **Cs** 132.91	Barium 56 **Ba** 137.33	57-70 *	Lutetium 71 **Lu** 174.97	Hafnium 72 **Hf** 178.49(2)	Tantalum 73 **Ta** 180.95	Tungsten 74 **W** 183.84	Rhenium 75 **Re** 186.21	Osmium 76 **Os** 190.23(2)	Iridium 77 **Ir** 192.22	Platinum 78 **Pt** 195.08	Gold 79 **Au** 196.97	Mercury 80 **Hg** 200.59	Thallium 81 **Tl** 204.38	Lead 82 **Pb** 207.2	Bismuth 83 **Bi** 208.98	Polonium 84 **Po** [208.98]	Astatine 85 **At** [209.99]	Radon 86 **Rn** [222.02]
Francium 87 **Fr** [223.02]	Radium 88 **Ra** [226.03]	89-102 **	Lawrencium 103 **Lr** [262.11]	Rutherfordium 104 **Rf** [265.12]	Dubnium 105 **Db** [268.13]	Seaborgium 106 **Sg** [271.13]	Bohrium 107 **Bh** [270]	Hassium 108 **Hs** [277.15]	Meitnerium 109 **Mt** [276.15]	Darmstadtium 110 **Ds** [281.16]	Roentgenium 111 **Rg** [280.16]	Copernicium 112 **Cn** [285.17]	Ununtrium 113 **Uut** [284.18]	Flerovium 114 **Fl** [289.19]	Ununpentium 115 **Uup** [288.19]	Livermorium 116 **Lv** [293]	Ununseptium 117 **Uus** [294]	Ununoctium 118 **Uuo** [294]

*lanthanoids	Lanthanum 57 **La** 138.91	Cerium 58 **Ce** 140.12	Praseodymium 59 **Pr** 140.91	Neodymium 60 **Nd** 144.24	Promethium 61 **Pm** [144.91]	Samarium 62 **Sm** 150.36(2)	Europium 63 **Eu** 151.96	Gadolinium 64 **Gd** 157.25(3)	Terbium 65 **Tb** 158.93	Dysprosium 66 **Dy** 162.50	Holmium 67 **Ho** 164.93	Erbium 68 **Er** 167.26	Thulium 69 **Tm** 168.93	Ytterbium 70 **Yb** 173.05
**actinoids	Actinium 89 **Ac** [227.03]	Thorium 90 **Th** 232.04	Protactinium 91 **Pa** 231.04	Uranium 92 **U** 238.03	Neptunium 93 **Np** [237.05]	Plutonium 94 **Pu** [244.06]	Americium 95 **Am** [243.06]	Curium 96 **Cm** [247.07]	Berkelium 97 **Bk** [247.07]	Californium 98 **Cf** [251.08]	Einsteinium 99 **Es** [252.08]	Fermium 100 **Fm** [257.10]	Mendelevium 101 **Md** [258.10]	Nobelium 102 **No** [259.10]