**Mini Mock Exam**

**CHE-2C2Y COURSE TEST 2**

Name: ____________________________________

There are five little random questions in this booklet from the entire course.

Read through the question carefully and answer in full.

No cheating!

| **Question** | **Maximum Mark** (%) | **Your Mark** (%) |
|---|---|---|
| 1 | 20 | |
| 2 | 20 | |
| 3 | 20 | |
| 4 | 20 | |
| 5 | 20 | |
| | **Total Percentage** | |

**Question 1**

**Thermodynamics I**

1. Calculate $\Delta S$, $\Delta S_{surr}$ and $\Delta S_{tot}$ for:

(a) the isothermal, reversible expansion

(b) the isothermal, free expansion

of one mole of ideal gas molecules from 8.00 L to 20.00 L and 292 K. Explain any differences between the two paths.

[20%]

Model Answer

(a) $\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)$ **(4%)**

$\Delta S = 1\ x\ 8.314\ x\ \ln\left(\frac{8.00}{20.00}\right)$ = + 7.618 J $K^{-1}$ **(4%)**

$\Delta S_{surr}$ = - 7.618 J $K^{-1}$

*and*

$\Delta S_{tot}$ = 0 J $K^{-1}$ **(4%)**

(b) $\Delta S$ = + 7.618 J $K^{-1}$

*and*

$\Delta S_{surr}$ = 0 J $K^{-1}$

*and*

$\Delta S_{tot}$ = + 7.618 J $K^{-1}$ **(3%)**

Entropy is a state function so the change in entropy of the system is the same in all cases. For (a) $\Delta U$ = 0 so q = -w. The heat that flows out of the system flows into the surroundings. For (b), in a free expansion, no work is done. In which case w = o. As $\Delta U$ = 0 no heat is transferred to the surroundings. **(5%)**

**Question 2**

**Thermodynamics 2**

2. a. Draw a pressure – temperature phase diagram for a single component mixture ensuring that you show any phase boundaries and label the triple point, critical point, and region of supercritical fluid.

[10%]

b. At 276 K the osmotic pressure of a protein solution is 172 N $m^{-2}$. The concentration is 1 g in 200 $cm^3$ of solution. Assuming ideal behaviour calculate:

i. the concentration of the protein in mol $m^{-3}$

[5%]

ii. the molar mass of the protein in g $mol^{-1}$

[5%]

<u>Model Answer</u>

(a) **See diagram on next page for reference**

Label axis correctly, and drawing lines in correct places and placing solid, liquid and gas (S, L, G) in the correct places **(4%)**

<u>Labelling phase boundaries correctly:</u>

Solid/Liquid: Melting/Fusion & Freezing **(1%)**

Liquid/Gas: Vaporisation & Condensation **(1%)**

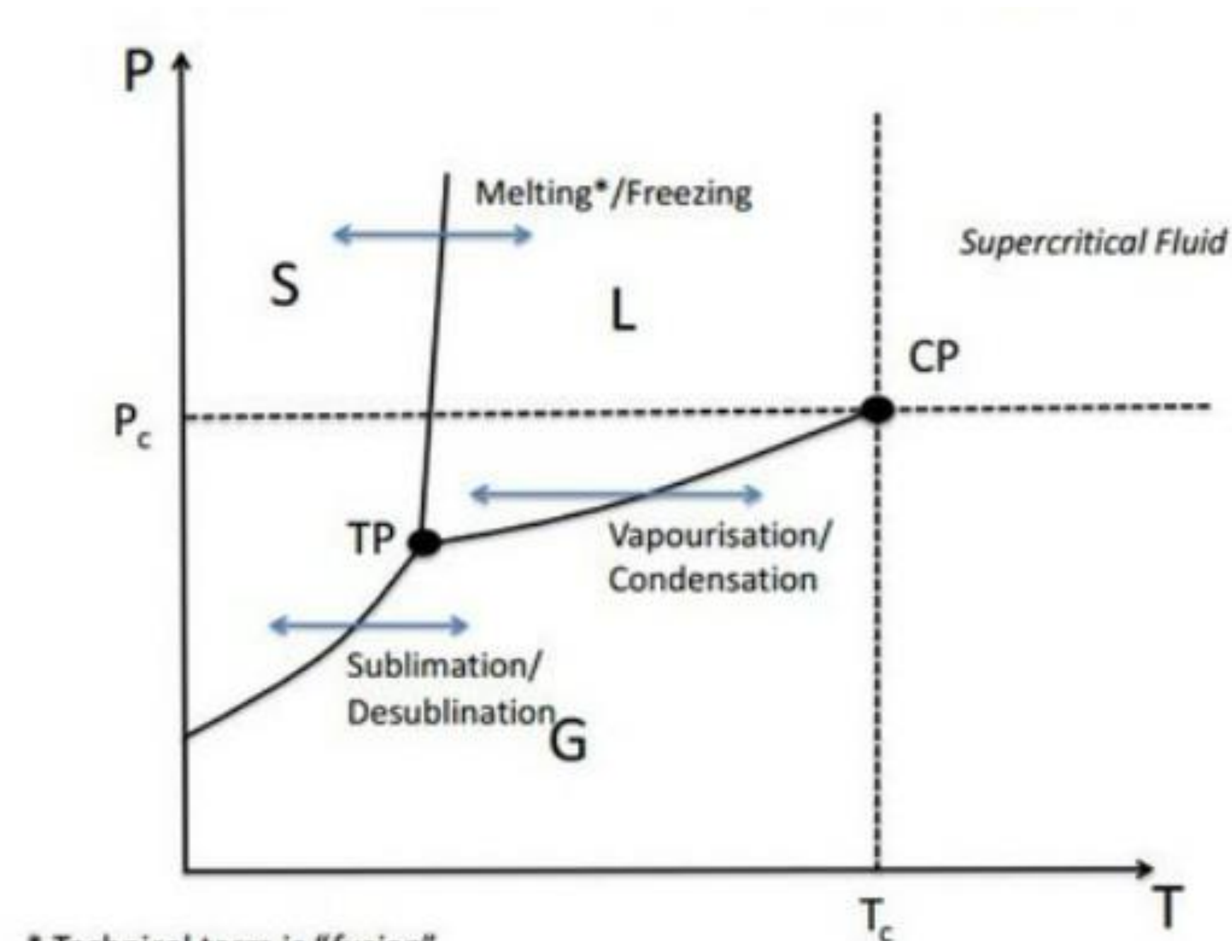
Gas/Solid: Sublimation/Desublimation **(1%)**

<u>Labelling of the significant points on the diagram:</u>

Triple Point **(1%)**

Critical Point **(1%)**

Supercritical Fluid **(1%)**




(b)

(i) $\pi = RTc_{solute}$ $\quad$ *therefore* $\quad$ $c_{solute} = \frac{\pi}{RT}$ **(3%)**

$$c_{solute} = \frac{\pi}{RT} = \frac{172}{8.314\ x\ 276} = 0.075\ mol\ m^{-3}$$ **(2%)**

(ii) $c_{solute} = \frac{mass_{sucrose}}{MM_{sucrose}\ x\ volume_{solution}}$ **(3%)**

Therefore $MM_{sucrose} = \frac{mass_{sucrose}}{c_{sucrose}\ x\ volume_{solution}} = \frac{1}{200\ x\ 10^{-6}\ x\ 0.075} = 66.7\ x\ 10^3 g\ mol^{-1}$ **(2%)**

**Question 3**

**Complex Kinetics**

3. The following Rice-Herzfeld mechanism is shown:

| | | |
|---|---|---|
| $CH_3CHO \rightarrow CH_3^{\bullet} + CHO^{\bullet}$ | $k_1$ | ☐ |
| $CH_3CHO + CH_3^{\bullet} \rightarrow CH_3CO^{\bullet} + CH_4$ | $k_2$ | ☐ |
| $CH_3CO^{\bullet} \rightarrow CH_3^{\bullet} + CO$ | $k_3$ | ☐ |
| $2\ CH_3^{\bullet} \rightarrow C_2H_6$ | $k_4$ | ☐ |

a. Label which reaction steps are Initiation, Propagation and Termination steps by placing I, P or T respectively in the boxes.

[5%]

b. Apply a suitable approximation to show that the rate of formation of methane can be expressed as:

$$\frac{d[CH_4]}{dt} = k_2\sqrt{\frac{k_1}{2k_4}}[CH_3CHO]^{3/2}$$

[15%]

Model Answer

(a) $k_1$ : Initiation

$k_2$ & $k_3$: Propagation

$k_4$: Termination **(5%)**

(b)

$\frac{d[CH_4]}{dt} = k_2[CH_3CHO][CH_3^{\cdot}]$ **(2%)**

$CH_3^{\bullet}$, $CHO^{\bullet}$ and $CH_3CO^{\bullet}$ are intermediates

<u>Apply SSA to rate equation of $CH_3^{\bullet}$</u> **(3%)**

$$\frac{d[CH_3^{\cdot}]}{dt} = k_1[CH_3CHO] - k_2[CH_3CHO][CH_3^{\cdot}] + k_3[CH_3CO^{\cdot}] - 2k_4[CH_3^{\cdot}]^2 = 0$$

<u>Apply SSA to rate equation of $CH_3CO^{\bullet}$</u> **(3%)**

$$\frac{d[CH_3CO^{\cdot}]}{dt} = k_2[CH_3CHO][CH_3^{\cdot}] - k_3[CH_3CO^{\cdot}] = 0$$

<u>As the two are equal to zero they can be placed equal to one another:</u> **(2%)**

$$k_1[CH_3CHO] - k_2[CH_3CHO][CH_3^{\cdot}] + k_3[CH_3CO^{\cdot}] - 2k_4[CH_3^{\cdot}]^2 = k_2[CH_3CHO][CH_3^{\cdot}] - k_3[CH_3CO^{\cdot}]$$

<u>This cancels to give</u>: **(2%)**

$$k_1[CH_3CHO] - 2k_4[CH_3^{\cdot}]^2 = 0$$

<u>And rearranged to give:</u> **(2%)**

$$[CH_3^{\cdot}] = \sqrt{\frac{k_1}{2k_4}[CH_3CHO]}$$

<u>Inserted into the original equation to give the final answer:</u> **(1%)**

$$\frac{d[CH_4]}{dt} = k_2\sqrt{\frac{k_1}{2k_4}}[CH_3CHO]^{3/2}$$

**Question 4**

**Theories of Chemical Reactions**

4. a. In a temperature jump the relaxation time, τ, is measured. Show that for the reaction

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$

the relaxation time is given by

$$\frac{1}{\tau} = \{k_1([\bar{A}] + [\bar{B}]) + k_{-1}([\bar{C}] + [\bar{D}])\}$$

[10%]

b. For an ion combination reaction, $A^+ + B^- \rightarrow AB$, calculate $d_{eff}$ with a dielectric constant of 80.

$d_{AB} = 4 \times 10^{-10}$ *m*, $e = 1.6 \times 10^{-19}$ *C*, $\varepsilon_0 = 8.85 \times 10^{-12}\ J^{-1}\ C^2\ m^{-1}$,

$k_B = 1.38 \times 10^{-23}\ J\ K^{-1}\ mol^{-1}$, $T = 300\ K$

[10%]

Model Answer

(a)

$$-\frac{d[A]}{dt} = k_1[A][B] - k_{-1}[C][D]$$ **(1%)**

$$-\frac{d[\bar{A}]}{dt} = k_1[\bar{A}][\bar{B}] - k_{-1}[\bar{C}][\bar{D}]$$ **(1%)**

$$-\frac{d([\bar{A}]+\Delta x)}{dt} = k_1(([\bar{A}] + \Delta x)([\bar{B}] + \Delta x) - k_{-1}(([\bar{C}] - \Delta x)([\bar{D}] - \Delta x)$$

**(2%)**

$-\frac{d[\bar{A}]}{dt}+\frac{\Delta x}{dt}=k_1\{[\bar{A}][\bar{B}]+\Delta x[\bar{A}]+\Delta x[\bar{B}]+\Delta x^2\}-k_{-1}\{[\bar{C}][\bar{D}]-\Delta x[\bar{C}]-\Delta x[\bar{D}]+\Delta x^2\}$ **(2%)**

Any term that does not contain $\Delta$x or contains $\Delta x^2$ is eliminated

$\frac{\Delta x}{dt}=k_1\{\Delta x[\bar{A}]+\Delta x[\bar{B}]\}-k_{-1}\{-\Delta x[\bar{C}]-\Delta x[\bar{D}]\}$ **(2%)**

This is rearranged: **(1%)**

$$\frac{\Delta x}{dt}= \Delta \mathrm{x}\left\{\{k_1([\bar{A}]+[\bar{B}])+k_{-1}([\bar{C}]+[\bar{D}])\}\right\}$$

And therefore the time constant is given as: **(1%)**

$$\frac{1}{\tau}= \{k_1([\bar{A}]+[\bar{B}])+k_{-1}([\bar{C}]+[\bar{D}])\}$$

(b)

$\delta=\frac{Z_A Z_B e^2}{4\pi\varepsilon_0\varepsilon_r d_{AB} k_B T}$ **(3%)**

$=\frac{+1\ x{-1}\ x\ 1.6\ x\ 10^{19^2}}{4\pi\ x\ 8.85\ x\ 10^{-12} x\ 80\ x\ 4\ x\ 10^{-10} x\ 1.38\ x\ 10^{-23}\ x\ 300}=1.738$ **(2%)**

$d_{eff}=d_{AB}\left(\frac{\delta}{e^{\delta}-1}\right)$ **(3%)**

$4\ x\ 10^{-10}\left(\frac{1.738}{e^{1.738}-1}\right)=1.484\ x\ 10^{-10} m$ **(3%)**

**Question 5**

**Surface Chemistry**

5. a. When contained in the cylindrical pores of a porous material the vapour pressure of $CO_2$ drops from the normal vapour pressure at 25 °C of 64.0 bar to a lower value of 62.0 bar. Estimate the pore size of the porous material.

Take the molar volume of $CO_2$ at 25 °C to be 61.6 $cm^3$ $mol^{-1}$ and the surface tension to be 1.16 mN $m^{-1}$, R = 8.314 J $K^{-1}$ $mol^{-1}$.

[15%]

b. The chemisorption of a gas is described by the Languir isotherm with K = 8.5 x $10^{-4}$ $Pa^{-1}$. What gas pressure would be required to obtain a surface coverage of 0.5?

[5%]

Model Answer

(a)

$ln\left(\frac{P_{vap}}{P_{vap}^{0}}\right) = \frac{V_m}{RT}\frac{2\gamma}{r}$ **(5%)**

Rearrange to give: **(5%)**

$$\frac{RTln\left(\frac{P_{vap}}{P_{vap}^{0}}\right)}{V_m 2\gamma} = \frac{1}{r} \quad therefore \quad r = \frac{V_m 2\gamma}{RTln\left(\frac{P_{vap}}{P_{vap}^{0}}\right)}$$

Substitute in numbers: **(5%)**

$$r = \frac{V_m 2\gamma}{RTln\left(\frac{P_{vap}}{P_{vap}^{0}}\right)} = \frac{61.6\ x\ 10^{-6}\ x\ 2\ x\ 1.16\ x\ 10^{-3}}{8.314\ x\ 298\ x\ ln\left(\frac{62.0}{64.0}\right)} = -1.817\ x\ 10^{-9} m$$

(b)

Langmuir isotherm

$\theta = \frac{KP}{1+KP}$ **(2%)**

Rearrange to make pressure the subject

$P = \frac{\theta}{K-K\theta}$ **(2%)**

Substitute in numbers

$\frac{\theta}{K-K\theta} = \frac{0.5}{8.5\ x\ 10^{-4}-(0.5\ x\ 8.5\ x\ 10^{-4})} = 1176\ Pa$ **(1%)**

**END OF PAPER**