

Mid Sem-I

CHM202: Energetics and Dynamics of Chemical Reactions

Date (Day): 04-Feb-2019 (Monday)

Total marks: 15

Time: 1 hour

Useful relations:

$$\left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P + V = -C_P \mu_{JT}$$

1. Consider a process in which pressure is not constant throughout the entire process, but for which the final and initial pressures are equal. Need enthalpy be equal to heat change here? Justify. 1

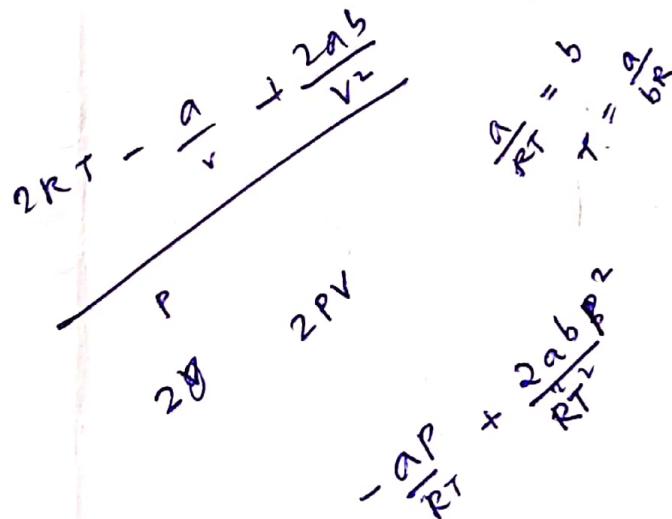
2. What will be the efficiency of a Carnot engine using oxygen (mol wt: 32) with respect to another Carnot engine that uses nitrogen (mol wt: 28)? Justify. 1

3. To calculate entropy of the surroundings, why only heat change is considered irrespective of whether the heat change was done reversibly or not? 1

✓ 3. Show that the area enclosed by the Carnot cycle on a temperature versus entropy diagram is equal to the work done. 2

✓ 4. Consider a system consisting of 1.5 mol CO₂(g), initially at 15°C and 9.0 atm and confined to a cylinder of cross-section 100.0 cm². The sample is allowed to expand adiabatically against an external pressure of 1.5 atm until the piston has moved outwards through 15 cm. Assume that carbon dioxide may be considered a perfect gas with $\bar{C}_V = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$, and calculate (a) \underline{Q} , (b) \underline{W} , (c) ΔU , (d) ΔT , (e) ΔS . 5

6. Show that the Joule-Thompson coefficient for 1 mole of a van der Waals gas is $\frac{1}{C_P} \left[\frac{2a}{RT} - \frac{3abP}{R^2T^2} - b \right]$. (Hint: Ignore $\frac{1}{V^2}$ and $\frac{1}{V^3}$ terms compared with P and approximate $P\bar{V} \approx RT$). 5



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10 1/2

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1/ For a cyclic process, $P_{initial} = P_{final}$

We know, $H = \cancel{U} + PV$
 $\rightarrow \Delta H = \Delta U + \Delta(PV)$
 $\Rightarrow \Delta H = \cancel{\Delta PV}$
 $= -dW + V dP$

For a cyclic process
 $\Delta U = 0$

Now, $dU = dQ + dW$
 $\rightarrow dQ = -dW$

Heat change need not be equal to enthalpy change.

✓ ①

— X —

2/ The efficiency of both the engine will be the same as efficiency depends on the temperature of reservoir and sink and not the material of the engine

$$\eta = 1 - \frac{T_c}{T_h} \quad \checkmark \quad \textcircled{1}$$

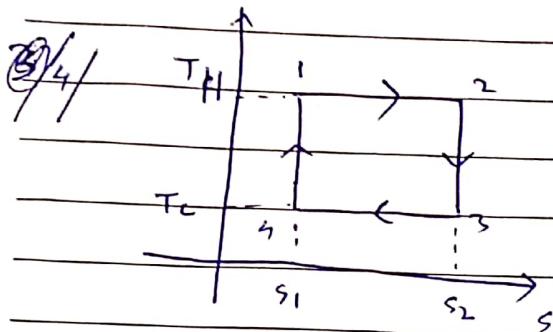
— X —

3/ Entropy of the system defined as $\frac{dQ_{rev}}{T}$

but entropy of surroundings defined as $\frac{dQ}{T}$

Also, This also made it possible for $\Delta S_{total} > 0$ for any process.

Therefore, heat change is only required for calculating entropy of surroundings irrespective of the fact the process is reversible or irreversible



We know

$$W = W_{12} + W_{23} + W_{34} + W_{41}$$

~~W₁₂~~

$1 \rightarrow 2$

$2 \rightarrow 3$

$$dV = d\theta + dW$$

$$dW = dV$$

$$\Rightarrow 0 = d\theta + dW$$

$$W_{23} = c_v (T_c - T_H)$$

$$\Rightarrow -d\theta = dW$$

$$\Rightarrow dW = -T ds$$

$2 \rightarrow 1$

$$W_{12} = -T_H (S_2 - S_1)$$

$$dW = dV$$

3 - 4

$$\Rightarrow W_{41} = c_v (T_H - T_c)$$

$$dW = -T_c (S_1 - S_2)$$

$$W_{34} = T_c (S_2 - S_1)$$

Now, $|W| = |(T_c - T_H)(S_2 - S_1)| \theta$

And Area of the graph $= (T_H - T_c)(S_2 - S_1)$

$\therefore |W| = \text{Area of the graph}$ ✓

(2)

s) (a) \therefore The process is adiabatic

$$Q = 0$$

(1)

✓

$$\cdot P = F/A$$

w =

$$(b) W = -PdV$$

$$= -1.5 \times 10^5 \times 15 \times 10^{-2} \times 100 \times 10^{-4} \text{ J}$$

$$= -1.5 \times 15 \times 10$$

$$= -225 \text{ J}$$

(1)

✓

$$(c) dU = dQ + dW$$

$$\bar{C}_V = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Rightarrow \Delta U = \cancel{dQ} + dW$$

$$\Rightarrow \cancel{dW} = -225 \text{ J}$$

(1)

$$\Rightarrow \Delta U = -225 \text{ J}$$

(d) we know

$$\Delta U = nC_V \Delta T$$

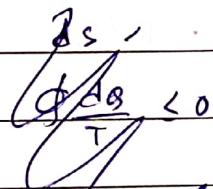
$$\Rightarrow \frac{-225}{nC_V} = \Delta T$$

$$\Rightarrow \frac{-225}{28.8 \times n} = \Delta T$$

$$\Rightarrow \Delta T = -7.81 \text{ K} \quad \times 0$$

(e) ~~$\Delta S \geq 0$~~ $\Delta S \geq 0$ ~~$\Delta S = 0$~~
 ~~\therefore Process is irreversible~~

we know ΔS_{total}



$$(e) \Delta S = 0$$

Although the process is irreversible, we can always find an reversible adiabatic path and calculate ΔS from it. They give the same answer as S is a state function

$\times 0$

Q/

$$\textcircled{a} \quad \left(P + \frac{a}{V^2} \right) (V - b) = RT$$

$$\Rightarrow P = \frac{RT}{V-b} - \frac{a}{V^2}$$

Given

$$\left(\frac{\partial H}{\partial P} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_P + V = -c_p \mu_{VT}$$

Q/

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT$$

$$\Rightarrow PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT \quad \text{--- } \textcircled{a} \textcircled{x}$$

$$\Rightarrow P dV + \frac{a}{V^2} dV - 0 + \frac{2ab}{V^3} dV = R dT$$

$$\Rightarrow \left(P - \frac{a}{V^2} + \frac{2ab}{V^3} \right) \frac{dV}{dT} = R$$

~~$$\Rightarrow \left(\frac{dV}{dT} \right)_P = \frac{R}{P}$$~~

$$\Rightarrow \left(\frac{dV}{dT} \right)_P = \frac{R}{\left(P - \frac{a}{V^2} + \frac{2ab}{V^3} \right)}$$

$$\therefore c_p \mu_{VT} = \frac{-RT}{\left(P - \frac{a}{V^2} + \frac{2ab}{V^3} \right)} + V$$

$$= -RT + PV - \frac{a}{V} + \frac{2ab}{V^2}$$

$$P - \frac{a}{V^2} + \frac{2ab}{V^3}$$



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$$\Rightarrow -c_p u_{JT} = -\frac{a}{V} + \frac{2ab}{V^2}$$

Approximation
 $PV \approx RT$

$$\Rightarrow -c_p u_{JT} = \frac{1}{P} \left[-\frac{aP}{RT} + \frac{2abP^2}{R^2T^2} \right]$$

$$\Rightarrow \textcircled{*} u_{JT} = \frac{1}{c_p} \left[\frac{aP}{RT} - \frac{2abP^2}{R^2T^2} \right]$$

$PV = \frac{RT}{bR}$

Putting RT value from $\textcircled{*}$

$$\Rightarrow - \left(PV + \frac{a}{V} - Pb - \frac{ab}{V^2} \right) + PV - \frac{a}{V} + \frac{2ab}{V^2} = -c_p u_{JT}$$

P

$$\Rightarrow \frac{-2a}{V} + Pb + \frac{3ab}{V^2} = -c_p u_{JT}$$

Approximate
 $PV \approx RT$

$$\Rightarrow \textcircled{*} \left[\frac{2a}{RT} - \frac{3abP}{R^2T^2} - b \right] = c_p u_{JT}$$

$$\Rightarrow u_{JT} = \frac{1}{c_p} \left[\frac{2a}{RT} - \frac{3abP}{R^2T^2} - b \right]$$

A 1/2

✓

X

Mid Sem-II

CHM202: Energetics and Dynamics of Chemical Reactions

Date (Day) & Hours: 13-Mar-2019 (Wed) & 12:00 to 13:00

Total marks: 15

Time: 1 hour

Useful relations:

$$dU = TdS - PdV \text{ (for reversible process)}$$

$$dH = n \times C_p \times dT \text{ (for ideal gas)}$$

$$\Delta T_f = K_f \times b \text{ (where } b \text{ is molality)}$$

$$K_p = \prod_j a_j^{v_j} = \prod_j \left(\frac{P_j}{P_0} \right)^{v_j} \text{ (for a gas phase reaction)}$$

1. Give examples of one second-order and one first order phase transitions. 1
2. One mole of an ideal monatomic gas is taken reversibly from 500K, 1 atm to 600K, 2 atm. Calculate ΔG for the process. Given: $\bar{S}_{298}^0 = 5 J^{-1} K^{-1} mol^{-1}$. 5
3. An aqueous solution contains 5% by weight of glucose and 10% by weight of sodium chloride. What will be its freezing point? Given: $K_f = 1.86 \text{ } ^\circ\text{C.g.mol}^{-1}$. 3
4. If α is the degree of formation of PCl_5 from PCl_3 at pressure P , find α in terms of P and equilibrium constant K_p . 3
5. Derive a relation for half life of a reaction for which the observed rate varies with n^{th} ($n \neq 1$) power of concentration of one of the reactants. 3

$$\begin{aligned} & A^2 - A^2 \times 2^\alpha P \times A \times 2^\alpha \\ & (2^\alpha - 1) A \times 2^\alpha \end{aligned}$$

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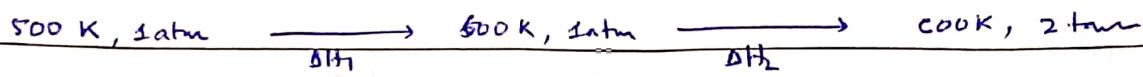
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- 1/ ~~1~~- first order phase transition — boiling of water ✓
 second order phase transition — sublimation of CO_2 ✓

~~X~~

— X —

2/ ~~2~~ $c_v = \frac{3}{2} R$



$$\begin{aligned}\Delta H_1 &= c_p \Big|_{T_1}^{T_2} \\ &= \frac{5}{2} R \ln \frac{600}{500} \\ &= 250 R = 2078.5 \text{ J}\end{aligned}$$

$\Delta H_2 = 0$: isothermal process

~~A1~~

$$\Delta S_1 = c_v \int \frac{dT}{T} - R \int \frac{dp}{P}$$

$$\begin{aligned}S_1 - S_0 &= c_v \ln \frac{500}{273} - R \ln \frac{500}{273} \\ &= c_v \ln \frac{500}{273} \\ &= c_v \ln 1.677\end{aligned}$$

$$\begin{aligned}S_1 &= 1.677 c_v + S_0 = 0.517 c_v + S_0 \\ &= 6.447 + 5 = 11.447 \text{ J}^{-1} \text{ K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}S_2 - S_0 &= c_v \int \ln \frac{600}{273} - R \ln^2 \frac{600}{273} \\ &= 0.699 c_v - R \cdot 0.693 R\end{aligned}$$

Now,

$$T_1 S_1 = 5723.5$$

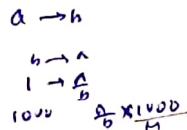
$$S_2 = 0.699 c_v - 0.693 R + S_0$$

$$T_2 S_2 = 4773.6$$

F

$$= 8.717 - 5.761 + 5$$

$$= 7.952 \text{ J K}^{-1} \text{ mol}^{-1}$$



$$\Delta G_r = \Delta H - \Delta(T_S)$$

$$= \Delta H - T_2 \cdot S_2 + T_1 \cdot S_1$$

$$= 2078.5 - 4773.6 + 5723.5$$

$$= 3028.4 \text{ J}$$

~~✓~~

— X —

3/ Let mass of water = 1kg = 1000 g

~~(100)~~

no. moles of glucose = $\frac{100}{\frac{180}{100} \times 1000} = \frac{500}{180} = \frac{5}{18} = 0.2778$

mole of NaCl = $\frac{\frac{100}{100} \times 1000}{58.5} = \frac{100}{58.5} = 1.709$

Molality = $\frac{\text{no. of moles}}{\text{Mass of soln}} = 1.709 + 0.2778 \quad K_f = 1.86 \text{ } ^\circ\text{C g mol}^{-1}$
~~Mass of soln~~
 $= 1.9868 \text{ m} \quad = 1.86 \times 10^{-3} \text{ } ^\circ\text{C kg mol}^{-1}$

$\therefore \Delta T_f = K_f m$

$= \frac{1.86}{10^3} \therefore 1.9868$

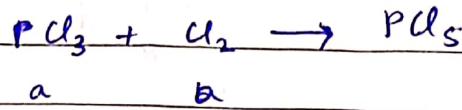
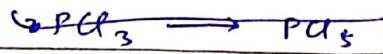
P3

$0^\circ\text{C} - T_f = 3.695 \times 10^{-3}$

$\Rightarrow T_f = \cancel{0^\circ\text{C}} - 3.695 \times 10^{-3} \text{ } ^\circ\text{C}$

~~✓~~

3/



chlorine is excess
left over

Partial pressure	$\frac{a - \alpha x}{a + \alpha x} p$	$\frac{a - \alpha x}{a + \alpha x} p$	$\frac{\alpha x}{a + \alpha x} p$
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$$K_p = \prod_i a_i^{v_i}$$

$$K_p = \left(\frac{P_{\text{PCl}_5}}{P_0} \right) \checkmark$$

$$\Rightarrow K_p = \left(\frac{P_{\text{PCl}_5}}{P_0} \right) \left(\frac{P_{\text{Cl}_2}}{P_0} \right)^{-1} \left(\frac{P_{\text{PCl}_3}}{P_0} \right)^{-1}$$

$$\Rightarrow K_p = \left(\frac{\alpha x P_0}{P_0(2a - \alpha x)} \right) \left(\frac{(a - \alpha x) P_0}{P_0(2a - \alpha x)} \right)^{-1} \left(\frac{P_0}{P_0} \right) \left(\frac{a - \alpha x}{2a - \alpha x} \right)^{-1}$$

$$\Rightarrow K_p = \frac{\alpha}{(2 - \alpha)} \frac{(1 - \alpha)^{-1}}{(2 - \alpha)^{-1}} \frac{(1 - \alpha)^{-1}}{(2 - \alpha)^{-1}} \frac{P_0}{P_0} \quad \textcircled{A2}$$

$$\Rightarrow \frac{P}{P_0} K_p = \frac{\alpha(2 - \alpha)}{(1 - \alpha)^2} \quad \checkmark$$

$$\Rightarrow \frac{P}{P_0} K_p = \frac{2\alpha - \alpha^2}{(1 - \alpha)^2}$$

F1

$$\Rightarrow (1 + \alpha^2 - 2\alpha) \frac{P}{P_0} K_p = 2\alpha - \alpha^2$$

$$\Rightarrow A\alpha^2 - 2\alpha A + A - 2\alpha + \alpha^2 = 0 \quad \text{where } A = \frac{P}{P_0} K_p$$

$$\Rightarrow (A + 1)\alpha^2 - 2\alpha A + (A - 2\alpha) = 0$$

$$\Rightarrow (A + 1)\alpha^2 - 2(A + 1)\alpha + A = 0$$

$$\alpha = \frac{-2A \pm \sqrt{4(A+1)^2 - 4(A+1)(A)}}{2(A+1)} = \frac{A - \sqrt{A+1}}{A+1}$$

~~$$\alpha = \frac{-2A \pm \sqrt{(2\alpha-1)A+2\alpha}}{A+1}$$~~

20/2

9

$$-\frac{d[A]}{dt} = k[A]^n$$

$$\Rightarrow \frac{d[A]}{[A]^n} = -k dt$$

$$\Rightarrow \int_{[A]_0}^{[A]} \frac{d[A]}{[A]^n} = -k \int_0^t dt$$

~~Method~~

$$\Rightarrow \frac{1}{1-n} \left[\frac{1}{[A]^{n-1}} \right]_{[A]_0}^{[A]} = -k t$$

$$\Rightarrow \left(\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right) = (n-1) k t$$

Now,

$$\Rightarrow t_{1/2} = \left(\frac{2^{n-1}}{[A]_0^{n-1}} - \frac{1}{[A]_0^{n-1}} \right) \frac{1}{k(n-1)}$$

(*)

$$\Rightarrow t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}}$$

X

Ans A

$$\begin{aligned} & \text{Ans A} \\ & \theta = (\alpha_1 - \beta_1 + \gamma_1) + (\alpha_2 - \beta_2 + \gamma_2) + \dots \\ & \quad + (\alpha_n - \beta_n + \gamma_n) \\ & \theta = \alpha_1 + \alpha_2 + \dots + \alpha_n - (\beta_1 + \beta_2 + \dots + \beta_n) + (\gamma_1 + \gamma_2 + \dots + \gamma_n) \end{aligned}$$

$$\frac{\partial \theta}{\partial A} = (\alpha_1 - \beta_1 + \gamma_1) + (\alpha_2 - \beta_2 + \gamma_2) + \dots + (\alpha_n - \beta_n + \gamma_n)$$

$$(\alpha - \beta + \gamma)$$

$$(\alpha - \beta + \gamma)^2 + \theta$$

NOTE:

Answer ALL Questions.

You need to clearly show each step (how you arrive at the final answer).

Write units (for numerical problems).

Clearly label the axes and show the quantities in plots (questions #3 & #4).

5

1) Give one word/phrase answers to the following (no need to justify/explain):

- $(\partial T / \partial V)_S = ?$
- What will be the ratios of efficiencies of two Carnot engine using oxygen (mol wt: 32) and nitrogen (mol wt: 28)?
- What is the Joule-Thompson coefficient for an ideal non-linear triatomic gas?
- For a real solution, when Raoult's law is obeyed?
- Under what condition $dA_{sys} < 0$ denotes spontaneous process?
- For an elementary gas-surface phase bimolecular reaction, the Eley-Rideal mechanism says that the rate determining step involves reaction between two species. Which are those species?
- Express the critical temperature (T_c) in terms of van der Waals constants.
- According to classical equipartition theorem, molar heat capacity at constant volume (C_v) for one mole of a nonlinear triatomic gas molecule is:
- The rate law for the gas-phase reaction between hydrogen and bromine is found to be:

$$\frac{1}{2} \frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1+k'[HBr][Br]^{-1}}$$
. What is the order of the reaction with respect to Br?
- To get maximum yield of product for an endothermic reaction, why we need an minimal (optimal) temperature?

- 2) 5 moles of an ideal monatomic gas, initially at 500 K and 10 atm is allowed to expand adiabatically in two ways:

a) (reversibly) until the pressure falls to 5 atm and

b) (irreversibly) against a constant pressure of 1 atm until the pressure falls to 5 atm.

For each of these two processes, calculate the final temperature, work done, change in (internal) energy and enthalpy.

From the results, can you comment on the quantitative changes in temperature and work done in reversible vs irreversible processes? $4 + 4 + 1 = 9$

- 3) In class, we discussed the solution for the concentration of an intermediate B in a consecutive reaction of type $A \rightarrow B \rightarrow C$ with (first-order) rate constants k_1 and k_2 as: $[B(t)] = \frac{k_1}{k_2 - k_1} [A(0)] (e^{-k_1 t} - e^{-k_2 t})$. Plot $[B(t)]$ vs time for $k_1 \gg k_2$ and $k_1 \ll k_2$ with a brief discussion of the nature of the curves at early and late times. $3 + 3 = 6$

$$\frac{[B]_{\max}}{[B]_0} = \frac{1}{e^{k_1 t}} + \frac{\alpha}{\beta} = \frac{1}{e^{k_1 t}}$$

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End Sem Exam
 CHM202: Energetics and dynamics of chemical reactions
 23-April-2019/2 PM to 5 PM/LH5 & LH6
 Full marks: = 50

4) In two plots, qualitatively sketch the Lineweaver-Burk plots of enzyme catalyzed reaction with

a) competitive inhibition

b) non-competitive inhibition

for two different concentrations of inhibitor. Indicate the values of slope, X-intercept and Y-intercept. 5

5) a) A first order reaction is 25% complete in 20 mins. How long will it take to be 85% complete? Calculate the rate constant.

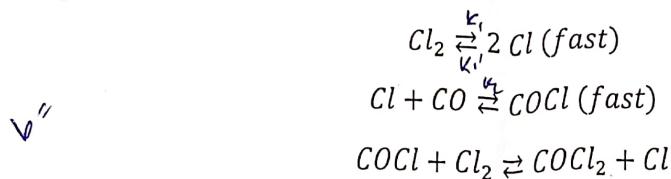
b) At 37°C , *Lactobacillus* in milk has a generation time of 69 mins. What is the population relative to initial population after 200 mins? $3 + 2 = 5$

6) The rate law for $\text{para-H}_2 \rightarrow \text{ortho-H}_2$ is: $d[\text{ortho-H}_2]/dt = k[\text{para-H}_2]^{3/2}$ Using two elementary reactions: (1) $\text{para-H}_2 \rightleftharpoons 2\text{H}$ and (2) $\text{H} + \text{para-H}_2 \rightarrow \text{H} + \text{ortho-H}_2$ derive the observed rate law.

The energies of activation of steps (1) and (2) are D_0 (the dissociation energy) and E_2 respectively. Show that the observed energy of activation is $E_{\text{observed}} = E_2 + D_0/2$. Also show for the pre-exponential factors that $A_{\text{observed}} = A_2 * (A_1/A_{-1})^{1/2}$. $3 + 1 = 4$

7) The enzyme-catalysed conversion of a substrate at 25°C has a Michaelis constant of 0.084 mol dm $^{-3}$. The rate of the reaction is 1.23×10^{-4} mol dm $^{-3}$ s $^{-1}$ when the substrate concentration is 0.45 mol dm $^{-3}$. What is the maximum velocity of this enzymolysis? 3

8) The possible mechanism of formation of phosgene is as follow:



Show that the decomposition of phosgene is 1st order with respect to COCl₂ and half order with respect to Cl₂. Take rate constants of individual steps according to your choice (for example, k_1 and k_{-1} for the first step). 3

9) Consider molecules that are confined to move in a plane (a two-dimensional gas). Calculate the distribution of speed and determine the most probable speed of the molecules at a temperature T.

All you need are:

1D Maxwell-Boltzman velocity distribution: $f(v_j)dv_j = Ae^{-bv_j^2}dv_j$ with $j = X/Y/Z$

Gamma function: $\int_0^\infty x^{n-1}e^{-ax}dx = \frac{\Gamma n}{a^n}$ with $\Gamma n = (n-1)!$ and $\Gamma \frac{1}{2} = \sqrt{\pi}$ $5 + 5 = 10$

$$\frac{1}{x} = \frac{1}{2}mv + \frac{KM}{2} \quad \left(\frac{1}{2}mv \right)^2 = \frac{v^2}{4m} \quad \frac{1}{x} = \frac{1}{2}mv + \frac{KM}{2} \quad \frac{1}{x} = \frac{1}{2}mv + \frac{KM}{2}$$

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Question: Using $\left(\frac{\partial P}{\partial \bar{V}}\right)_T = 0$ and $\left(\frac{\partial^2 P}{\partial \bar{V}^2}\right)_T = 0$ ($\bar{V} \equiv V_m$ is the molar volume) at critical point, evaluate the critical constants (P_c, \bar{V}_c, T_c) for a gas that obeys van der Waals equation of state. (You need to arrive at the expressions, don't just write the final answers!)

Answer: $\left(P + \frac{n^2 a^*}{V^2}\right)(V - nb) = nRT$ ✓

$$\Rightarrow \left(P + \frac{a}{V^2}\right)(\bar{V} - b) = RT \quad \checkmark$$

$$\Rightarrow P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \quad \checkmark$$

$$\left(\frac{\partial P}{\partial \bar{V}}\right)_T = -RT \left(\bar{V} - b\right)^2 + \frac{2a}{\bar{V}^3} = 0 \quad \left| \quad \left(\frac{\partial^2 P}{\partial \bar{V}^2}\right)_T = +2RT \left(\bar{V} - b\right)^3 - \frac{6a}{\bar{V}^4} = 0 \right.$$

$$\Rightarrow \frac{RT}{(\bar{V} - b)^2} = \frac{2a}{\bar{V}^3} \quad -\textcircled{I} \quad \Rightarrow \frac{2RT}{(\bar{V} - b)^3} = \frac{6a}{\bar{V}^4} \quad -\textcircled{II} \quad \checkmark$$

$$\textcircled{I}/\textcircled{II} \Rightarrow \frac{\frac{RT}{(\bar{V} - b)^2}}{\frac{2RT}{(\bar{V} - b)^3}} = \frac{\frac{2a}{\bar{V}^3}}{\frac{6a}{\bar{V}^4}}$$

$$\Rightarrow \frac{\bar{V} - b}{2} = \frac{\bar{V}}{3}$$

$$\Rightarrow \bar{V}_c = 3b \quad \checkmark$$

And

$$\Rightarrow \frac{RT_c}{(3b - b)^2} = \frac{2a}{(3b)^3}$$

$$\Rightarrow T_c = \frac{8a}{27bR}$$

$$P_c = \frac{R}{2b} \left(\frac{8a}{27bR} \right) - \frac{a}{9b^2}$$

$$= \frac{8a}{27b^2} - \frac{a}{9b^2}$$

$$= \frac{a}{27b^2}$$

✓

Total marks: 5

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Q1: Methane gas is heated from 25 °C until the volume has doubled. The pressure is constant at 1 bar. The variation in molar heat capacity with temperature has been measured and the results of those experiments can be summarized by the equation-

$$C_p = a + bT$$

$C_p = a + bT \times 10^{-3} \text{ JK}^{-2} \text{ mol}^{-1}$. Calculate ΔH and ΔU per mol.

4

where $a = 22.34 \text{ JK}^{-1} \text{ mol}^{-1}$ and $b = 48.1 \times 10^{-3} \text{ JK}^{-2} \text{ mol}^{-1}$. Assume the system follows the ideal gas behaviour.

Q2: Is it possible to find a point on the P-T phase diagram for carbon where graphite, diamond, liquid and vapour phase boundaries coincide? Justify. 1

Answer:

$$PV = nRT$$

$$\Rightarrow \frac{P_1}{R_1} = \frac{T_1}{V_1}$$

$$dH = C_p dT$$

$$dT = (a + bT)dT$$

$$\Delta H = aT_i + a(T_f - T_i) + \frac{b}{2}(T_f^2 - T_i^2)$$

$$\frac{T_1}{V_1} = \frac{T_2}{V_2}$$

$$= aT_i + \left(\frac{b}{2}\right) 3T_i^2$$

$$\frac{V_2}{V_1} = \frac{T_2}{T_1}$$

$$= 22.34 \times 298 + 24.05 \times 3 \times 10^{-3} \times (298)^2$$

$$\Rightarrow 2 = \frac{T_2}{T_1}$$

$$\approx 5687.32 \text{ J}$$

②

(1)

$$dU = d\theta + dW$$

$$dU = d\theta - PdV$$

$$\Delta U = \int d\theta - P \int dV$$

$$= \Delta H - 1(V_f - V_i)$$

$$= \Delta H - 2V_i$$

$$= \Delta H - \frac{2R}{2} \frac{298}{2}$$

$$= \Delta H - \frac{596R}{2} \text{ X0}$$

$$V_f = 2V_i$$

$$V_f - V_i = 2V_i - V_i$$

$$= V_i$$

$$\frac{22.34 \times 298}{298}$$

$$= 20106 \times \frac{4468 \times 2}{22573 \times 2}$$

$$\frac{298}{596}$$

PTO