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The values of fundamental constants and data relating to the questions on the examination can be found on this insert. You may use the back for scratch work but enter all work to be graded in the space provided with each question. Show your work in all questions involving computation in order to receive credit.

### **FUNDAMENTAL CONSTANTS**

$$R = 0.082054 \text{ L-atm/K-mol} = 8.31451 \text{ J/K-mol}$$

$$1 \text{ atm} = 101325 \text{ Pa}$$

$$F = 96485 \text{ C/mol}$$

$$h = 6.6261 \times 10^{-34} \text{ J-s}$$

$$k_B = 1.3807 \times 10^{-23} \text{ J/K-molec}$$

$$N_A = 6.02214 \times 10^{23} \text{ molec/mol}$$

atomic weights

$$\text{C} \quad 12.0 \text{ g/mol}$$

$$\text{H} \quad 1.0 \text{ g/mol}$$

### THERMODYNAMIC DATA FOR CARBON PHASES AT 298.15 K

<u>State</u>	<u><math>\Delta H_f^\circ</math>(kJ/mol)</u>	<u><math>\Delta S^\circ</math>(J/K-mol)</u>	<u><math>d</math>(g/cm<sup>3</sup>)</u>
solid, graphite	0	5.740	2.22
solid, diamond	1.895	2.377	3.51
liquid			1.37
gas	170.88	158.0	

solid(graphite)-liquid-gas triple point (TP)

$$T_{\text{TP}} = 4800 \pm 100 \text{ K}, \quad p_{\text{TP}} = 0.01 \text{ GPa (100 atm)}$$

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1) (70 points) The element carbon has several solid forms. The most common are graphite and diamond.

a) Under standard conditions what is the stablest solid form of carbon? Is this the case at both high and low temperatures? Briefly explain.

Under standard conditions (i.e. 1 atm pressure), graphite is the stablest solid form of carbon at all temperatures. It has the lowest standard enthalpy of formation and the highest standard entropy and therefore the lowest standard Gibbs free energy of formation. Please note, standard conditions refer to concentration. Despite what is suggested by elementary textbooks, there is no standard temperature! STP is a brand of motor oil.

b) Suggest conditions under which diamond is more stable?

Diamond with the higher density and the lower molar volume only becomes the stabler form under high pressure.

c) Will graphite melt under standard conditions? Briefly explain.

No. The pressure at the solid-liquid-gas critical point is above 1 atm so solid graphite when heated will sublime.

d) Estimate the vapor pressure in atm of solid graphite at 298 K.

For the reaction  $C(c) \rightarrow C(g)$   $K = p_C = \exp(-\Delta G^\circ/RT)$ .

$$\Delta H^\circ = 170.88 - 0 = 170.88 \text{ kJ} = 170880 \text{ J.}$$

$$\Delta S^\circ = 158.0 - 5.470 = 152.26 \text{ J/K.}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 170880 \text{ J} - (298.15 \text{ K})(152.26 \text{ J/K}) = 1.25 \times 10^5 \text{ J}$$

$$p_C = \exp\left\{-\frac{(1.25 \times 10^5 \text{ J})}{(298.15 \text{ K})(8.31451 \text{ J/K})}\right\} = \exp(-50.62)$$
$$= 1.0 \times 10^{-22} \text{ atm}$$

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2) (50 points) Li, Matthews, and Sinha [*Science*, 319, 1657-1660 (2008)]. recently discovered a new source for the hydroxyl radical in the troposphere. In their mechanism,  $\text{NO}_2$  absorbs light and becomes electronically excited. The excited species,  $\text{NO}_2^*$ , reacts with water to form OH.

a) The authors report that the rate of OH production varies linearly with the power of the laser used to excite the  $\text{NO}_2$ . What can be inferred from this observation?

The first step in the reaction is  $\text{NO}_2 + h\nu \rightarrow \text{NO}_2^*$ . A photon is a particle and this first step is a bimolecular process. Therefore, its rate is directly proportional to the concentration of photons which is measured by the power of the laser.

b) They employed pseudo first-order kinetics in their examination of the second step of the mechanism:  $\text{NO}_2^* + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{OH}$ . What condition must be satisfied in order to take this approach?

The concentration of water should be in large excess, i.e.  $[\text{H}_2\text{O}] \gg [\text{NO}_2^*]$ . This is straightforward since  $\text{NO}_2^*$  is an excited state, present at very low concentration.

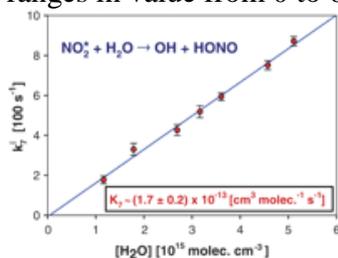
c) Suggest a structure of the activated complex for the second step in the mechanism.

The elementary step involves the transfer of a H atom from the water to the  $\text{NO}_2$ . A likely activated complex is  $\text{O-N-O}\cdots\text{H}\cdots\text{O-H}$  where  $\cdots$  denotes a partially formed or broken O, H bond.

d) Predict the signs of the entropy and enthalpy of activation for the second step.

The reaction pathway from reactants to the transition state involves bond breaking so the enthalpy of activation will be large and positive. The pathway involves combining 2 species to form one so the entropy of activation will also be positive.

e) The following figure from their paper shows the dependence of the pseudo first-order rate constant on the concentration of water. What conclusion can be drawn from the graph? Obtain a value of the bimolecular rate constant for the second step from the graph. The units of  $[\text{H}_2\text{O}]$  are in molecules/ $\text{cm}^3$ . The x-axis ranges in value from 0 to  $6 \times 10^{15}$ ; the y-axis, from 0 to  $10 \times 100 = 1000$ .

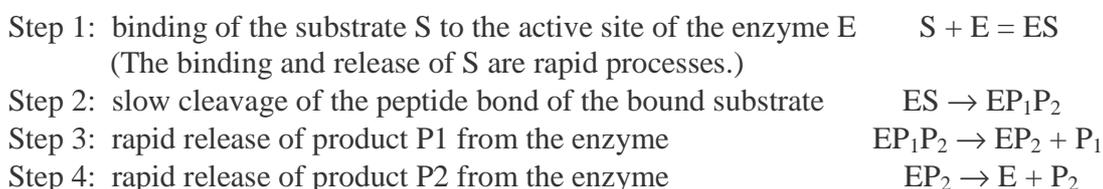


The graph shows the first-order dependence of the rate on  $[\text{H}_2\text{O}]$ .

$k^{(1)} = k_2[\text{H}_2\text{O}]$  so  $k_2$  is the slope of the graph.  $k_2 = \Delta k^{(1)} / \Delta[\text{H}_2\text{O}] = (10 \times 100 \text{ 1/s}) / (6 \times 10^{15} \text{ molec/cm}^3) = 1.7 \times 10^{-13} \text{ cm}^3/\text{molec}\cdot\text{s}$ .

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3) (30 points) Carboxypeptidase is an enzyme that catalyzes the breaking of the peptide bond. The following mechanism has been proposed for this reaction which has the net stoichiometry  $S \rightarrow P_1 + P_2$ . Derive the **empirical** rate law for the mechanism.



The net rate of the reaction is the rate of the slowest step, the second step in the mechanism. Hence,  $\text{Rate} = k_2[ES]$ . ES is an intermediate and its concentration must be expressed in terms of measureables, e.g. [S] and [E]. The binding and release of S to/from the enzyme occur so quickly that we can assume an equilibrium. That is,  $K_1 \cong [ES]/([S][E])$  so  $[ES] \cong K_1[E][S]$ . Therefore,  $\text{Rate} = k_2K_1[E][S]$ .

4) (50 points) Dobbs *et al.* employed quantum mechanics to calculate the bimolecular rate constant for the reaction of the hydroxyl radical with methane and reported the following values:  $4.98 \times 10^{-16}$  and  $1.6 \times 10^{-13} \text{ cm}^3/\text{molec}\cdot\text{s}$  at 200 and 400 K, respectively.

a) Calculate the Arrhenius activation energy for the forward reaction.

$$E_a \text{ is defined by a process, } E_a = -R\Delta \ln(k)/\Delta(1/T). \quad \ln(k_2) - \ln(k_1) = \ln(k_2/k_1)$$
$$E_a = -(8.314 \text{ J/K})\{\ln[(4.98 \times 10^{-16})/(1.6 \times 10^{-13})]\}/\{(1/200 \text{ K}) - (1/400 \text{ K})\} =$$
$$-(8.314)(-5.772)/(0.0025) = 19 \text{ kJ.}$$

b) Calculate the rms speed ( $v_{\text{rms}}$ ) of methane ( $\text{CH}_4$ ) at 400 K.

N.B. Use SI units throughout here! M is in kg/mole, not g/mole.

M for methane =  $12 + 4 \times 1 = 16 \text{ g./mole} = 0.016 \text{ kg/mole}$

$$v_{\text{rms}} = [\langle v^2 \rangle]^{0.5} = [(3RT)/M]^{0.5} = [(3)(8.314 \text{ J/K})(400 \text{ K})/(0.016 \text{ kg})]^{0.5}$$

$= [6.2 \times 10^5]^{0.5} = 790 \text{ m/s.}$  Note that at room temperature, the average translational kinetic energy,  $1.5RT$ , is much smaller than  $E_a$ . Very few collisions are successful.