

1. A reaction $A + B + C \rightarrow D$ follows the mechanism



in which the first step remains essentially in equilibrium. Show that the dependence of rate on temperature is given by

$$k = Ae^{-(E_a - \Delta H)/RT}$$

where ΔH is the enthalpy change for the first reaction.

(15%)

2. For a closed system containing C_2H_2 , H_2 , C_6H_6 , and $C_{10}H_8$, use a Gaussian elimination to obtain a set of independent chemical reactions.

(15%)

3. The pressure in interplanetary space is estimated to be of the order of 10^{-14} Pa. Calculate (a) the average number of molecules per cubic centimeter, (b) the collision frequency, and (c) the mean free path. Assume that only hydrogen atoms (diameter $d=0.2$ nm) are present and that the temperature is 1000 K.

(15%)

4. At pH 7 and pMg 4 what value of pCa is required to put half the ATP in the form $CaATP^{2-}$? At 0.2 mol L^{-1} ionic strength and 25°C the following constants are known:



(15%)

5. Derive the expression for $(\partial U / \partial V)_T$ (the internal pressure) for a gas obeying the van der Waals equation.

(15%)

6. (a) When an ideal gas is allowed to expand isothermally in a piston, $\Delta U = q + w = 0$. Thus, the work done by the system on the surroundings is equal to the heat transferred from the reservoir to the gas, and the efficiency of turning heat into work is 100%. Explain why this is not a violation of the second law. (6%)

(b) Explain what is the Joule-Thomson inversion temperature. (7%)

(c) Describe the osmosis phenomenon. (6%)

(d) Explain why the compressibility factor Z is below 1 at low pressure and above 1 at high pressure. (6%)