

## Assignment-IV

### B.Sc. Chem(Hons) I<sup>st</sup> year

### Semester II (2020)

### Unit- II<sup>nd</sup> Law of Thermodynamics

1. Calculate the entropy change when 0.5 dm<sup>3</sup> of an ideal gas ( $C_{v,m} = 12.6 \text{ JK}^{-1}\text{mol}^{-1}$ ) at 298K and 1 atm is allowed to expand to double its volume and simultaneously heated to 373 K.
2. One mole of van der Waal gas is allowed to expand isothermally and reversibly at 273 K from an initial volume of 1.0 dm<sup>3</sup> to 50.0 dm<sup>3</sup>. Calculate the entropy change for the gas. The van der Waals constants are  
a = 6.5 atm dm<sup>6</sup> mol<sup>-2</sup>, b = 0.056 dm<sup>3</sup> mol<sup>-1</sup>.
3. Two moles of an ideal gas are expanded isothermally at 298 K from a volume of V to 2.5 V. Find the value of  $\Delta S_{\text{gas}}$ , and  $\Delta S_{\text{total}}$  for the following;  
(a) Reversible expansion  
(b) Irreversible expansion when 400 J mol<sup>-1</sup> are less absorbed than in (a).  
(c) Free Expansion.
4. 1 mole of an ideal gas is allowed to expand isothermally at 27°C until its volume is tripled. Calculate  $\Delta S_{\text{sys}}$ , and  $\Delta S_{\text{univ}}$ , under the following conditions: (a) The expansion is carried out reversibly, (b) the expansion is a free expansion.
5. The molar entropy of an ideal gas ( $C_{p,m} = 20.9 \text{ JK}^{-1}\text{mol}^{-1}$ ) at 298K is 146.0 JK<sup>-1</sup>mol<sup>-1</sup>. Find its value at 500 K.

6. (a) Starting with the fundamental relations prove that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta}$$

Where  $\alpha = V^{-1}(\partial V/\partial T)_P$ ,  $\beta = -V^{-1}(\partial V/\partial P)_T$ .

- (b) For a given substance  $\alpha = 1.24 \times 10^{-3} \text{ K}^{-1}$  and  $\beta = 9.3 \times 10^{-5} \text{ atm}^{-1}$  at 290 K and 1 atm. Assuming  $\alpha$  and  $\beta$  to be constant, calculate the change in molar volume which should produce an entropy change of 2.1 JK<sup>-1</sup>mol<sup>-1</sup> at 290 K.

7. A gas obeying the equation of state  $P(V-B) = RT$  undergoes a change from the initial state  $T_1, V_1$  to a final state  $T_2, V_2$ . Derive an expression for the entropy change of this gas. The variation of heat capacity at constant volume is given by  $C_V = a + bT + cT^2$ .