

UNIVERSITY OF MALTA

DEPARTMENT OF CHEMISTRY

CH237 - Chemical Thermodynamics and Kinetics

Tutorial Sheet 4

- 1 (a) Calculate the change in entropy when 200 g of (i) water at 0°C, (ii) ice at 0°C is added to 200g of water at 90°C in an insulated container.

- (b) The molar heat capacity of lead varies with temperature as follows:

T/K	10	15	20	25	30	50
$C_{p,m} / (\text{JK}^{-1} \text{mol}^{-1})$	2.8	7.0	10.8	14.1	16.5	21.4
T/K	70	100	150	200	250	298
$C_{p,m} / (\text{JK}^{-1} \text{mol}^{-1})$	23.3	24.5	25.3	25.8	26.2	26.6

Calculate the standard Third-Law entropy of lead at (i) 0°C and (ii) 25°C.

- (c) The heat capacity of anhydrous potassium hexacyanoferrate(II) varies with temperature as follows:

T/K	$C_{p,m} / \text{JK}^{-1} \text{mol}^{-1}$	T/K	$C_{p,m} / \text{JK}^{-1} \text{mol}^{-1}$	T/K	$C_{p,m} / \text{JK}^{-1} \text{mol}^{-1}$
10	2.09	70	131.4	160	247.3
20	14.43	80	149.4	170	256.5
30	36.44	90	165.3	180	265.1
40	62.55	100	179.6	190	273.0
50	87.03	110	192.8	200	280.3
60	111.0	150	237.6		

Calculate the molar enthalpy relative to its value at $T = 0\text{K}$ and the Third-Law entropy at each of these temperatures. Plot graphs of these properties ($C_{p,m}$, etc.) vs. temperature.

- (d) Given that $S_m^0 = 29.79 \text{ JK}^{-1} \text{ mol}^{-1}$ for bismuth at 100 K and the following tabulated heat capacity data (D.G. Archer, *J. Chem. Eng. Data*, **40** (1995) p.1015), compute the standard molar entropy of bismuth at 200 K.

T/K	100	120	140	150	160	180	200
$C_{p,m} / (\text{JK}^{-1} \text{mol}^{-1})$	23.00	23.74	24.25	24.44	24.61	24.89	25.11

Compare this value to the value that would be obtained by taking the heat capacity to be constant at $24.44 \text{ JK}^{-1} \text{ mol}^{-1}$ over this range.

- 2 (a) *UoM, CH237, June 2001: This question discusses the dependence of various thermodynamic properties with temperature.*

(i) Show that enthalpy of formation and the molar entropy of a gas at a temperature T_2 in terms of their values at the same pressure at a temperature T_1 are given by:

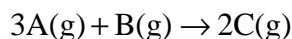
$$\Delta_f H^0(T_2) = \Delta_f H^0(T_1) + c_p (T_2 - T_1)$$

$$S_m^0(T_2) = S_m^0(T_1) + c_p \ln\left(\frac{T_2}{T_1}\right)$$

where c_p is the molar heat capacity at constant pressure, a constant for the temperature range $T_1 < T < T_2$.

(4 marks)

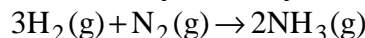
(ii) Using the expressions derived in (i), or otherwise*, write down an expression for $\Delta_r H^0$ and $\Delta_r S^0$ for the reaction:



at a temperature T_2 relative in terms of $\Delta_r H^0$ and $\Delta_r S^0$ at a temperature T_1 assuming that A, B and C are all gasses in the temperature range $T_1 < T < T_2$.

(4 marks)

(iii) Calculate the $\Delta_r H^0$ and $\Delta_r S^0$ for the reaction:



at 298K and 698K using the data from your data book. Use these values to obtain estimates of the Gibbs energy of formation of gaseous ammonia at the same temperatures. Comment on the results obtained.

(12 marks)

(*) *No marks will be deducted if the result is quoted rather than derived, provided that all the terms used are properly identified.*

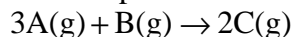
- (b) Derive expressions for the enthalpy of formation and the molar entropy of a gas at a temperature T_2 in terms of their values at the same pressure at a temperature T_1 assuming that for the temperature range $T_1 < T < T_2$, c_p is given by:

(i) $c_p = a + bT$

(ii) $c_p = a + bT + cT^2$

(iii) $c_p = a + bT + \frac{c}{T^2}$

and use these expressions to write down an expression for $\Delta_r H^0$ and $\Delta_r S^0$ for the reaction:



at a temperature T_2 relative in terms of $\Delta_r H^0$ and $\Delta_r S^0$ at a temperature T_1 assuming that A, B and C are all gasses in the temperature range $T_1 < T < T_2$.