

UNIVERSITY OF MALTA

DEPARTMENT OF CHEMISTRY

CH237 - Chemical Thermodynamics and Kinetics

Tutorial Sheet 5

- 1 (a) The standard enthalpy of combustion of solid phenol (C_6H_5OH) is -3054 kJmol^{-1} at 298 K and its standard molar entropy is $144.0 \text{ JK}^{-1} \text{ mol}^{-1}$. Calculate the standard Gibbs energy of formation of phenol at 298 K.
- (b) The standard enthalpy of combustion of solid urea ($CO(NH_2)_2$) is -632 kJmol^{-1} at 298 K and its standard molar entropy is $104.60 \text{ JK}^{-1} \text{ mol}^{-1}$. Calculate the standard Gibbs energy of formation of urea at 298 K.
- (c) Calculate the standard Gibbs energy of the reactions:
(a) $4HCl(g) + O_2(g) \rightarrow 2Cl_2(g) + 2H_2O(l)$
(b) $CO(g) + CH_3OH(l) \rightarrow CH_3COOH(l)$
from the standard entropies and enthalpies of formation.
- (d) (i) Calculate the standard reaction entropy at 298 K of:
(a) $2CH_3CHO(g) + O_2(g) \rightarrow 2CH_3COOH(l)$
(b) $2AgCl(s) + Br_2(l) \rightarrow 2AgBr(s) + Cl_2(g)$
(c) $Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)$
(ii) Combine these reaction entropies with the reaction enthalpies, and calculate the standard reaction Gibbs energies at 298 K.
(iii) Use standard Gibbs energies of formation to calculate the standard reaction Gibbs energies at 298 K of these reactions.
- (e) (i) Calculate the standard reaction entropy at 298 K of:
(a) $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
(b) $C_{12}H_{12}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$
(ii) Combine these reaction entropies with the reaction enthalpies, and calculate the standard reaction Gibbs energies at 298 K.
(iii) Use standard Gibbs energies of formation to calculate the standard reaction Gibbs energies at 298 K of these reactions.

- (f) The standard enthalpy of combustion of solid phenol ($\text{C}_6\text{H}_5\text{OH}$) and solid urea (NH_2CONH_2) are $-3054 \text{ kJ mol}^{-1}$ and -632 kJ mol^{-1} respectively at 298 K, and their standard molar entropy is $144.0 \text{ JK}^{-1} \text{ mol}^{-1}$ and $104.60 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively. Calculate the standard Gibbs energy of formation of (i) phenol and (ii) urea at 298 K.
- 2 (a) Calculate ΔG for the process where 3.0 mmol of nitrogen gas which initially occupies 36 cm^3 at 300 K expands to 60 cm^3 .
- (b) The change in the Gibbs energy for a certain constant pressure process was found to fit the expression $\Delta G(\text{J}) = -85.40 + 36.5 T(\text{K})$. Calculate ΔS for this process.
- (c) Calculate the change in Gibbs energy of 35 g of ethanol (mass density = 0.789 g cm^{-3}) when the pressure is increased isothermally from 1 atm to 3000 atm.
- (d) When 2.00 mol of a gas at 330 K and 3.50 atm is subjected to isothermal compression, its entropy decreases by 25.0 J K^{-1} . Calculate (i) the final pressure if the gas, and, (ii) ΔG for the compression.
- (e) Estimate the change in the Gibbs energy of 1 L liquid benzene when the pressure acting on it increases from 1 atm to 100 atm.
- (f) Calculate the maximum non-expansion work per mole that may be obtained from fuel cells in which the chemical reactions are the combustion of (i) methane, and, (ii) propane at 298 K.
- (g) Calculate the standard Helmholtz energy of formation, $\Delta_f A$ of liquid methanol at 298 K from the standard Gibbs energy of formation and the assumption that H_2 and O_2 are perfect gases.
- (h) Calculate (i) the maximum work and (ii) the maximum non-expansion work that can be obtained from the freezing of supercooled water at -5°C and 1 atm. The densities of water and ice are 0.999 g cm^{-3} and 0.917 g cm^{-3} , respectively, at -5°C .
- (i) The standard reaction Gibbs energy of:
- $$\text{K}[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}(\text{s}) \rightarrow 4\text{K}^+(\text{aq}) + [\text{Fe}(\text{CN})_6]^{4-}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$$
- is $+26.120 \text{ kJ mol}^{-1}$. (I.R. Malcolm, L.A.K. Staveley. And R.D. Worswick, *J. Chem. Soc. Faraday Trans. I*, (1973) p. 1532). The enthalpy of solution the trihydrate is $+55.000 \text{ kJ mol}^{-1}$. Calculate: (i) the standard molar entropy of the hexacyanoferrate(II) ion in water and (ii) the standard reaction entropy given that the standard molar entropy of the solid trihydrate is $599.7 \text{ JK}^{-1} \text{ mol}^{-1}$ and that of the K^+ ion in water is $102.5 \text{ JK}^{-1} \text{ mol}^{-1}$.

- (j) Nitric acid hydrates have received much attention as possible catalysts for heterogeneous reactions which bring about the Antarctic ozone hole. Worsnop *et al.* Investigated the thermodynamic stability of these hydrates under conditions typical of the polar winter stratosphere (D.R. Worsnop, L.E. Fox, M.S. Zahniser, and S.C. Wofsy, *Science* 259, 71 (1993)). They report thermodynamic data for the sublimation of mono-, di-, and trihydrates to nitric acid and water vapours,
 $\text{HNO}_3 \cdot n\text{H}_2\text{O}(\text{s}) \rightarrow \text{HNO}_3(\text{g}) + n\text{H}_2\text{O}(\text{g})$, $n = 1, 2, 3$. Given $\Delta_r G^0$ and $\Delta_r H^0$ for these reactions at 220 K, use the Gibbs Helmholtz equation to compute $\Delta_r G^0$ at 190 K.

n	1	2	3
$\Delta_r G^0 / (\text{kJ mol}^{-1})$	46.2	69.4	93.2
$\Delta_r H^0 / (\text{kJ mol}^{-1})$	127	188	237

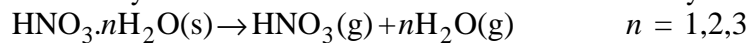
- (k) A sample of 1.00 mol of a monatomic perfect gas with $C_{V,m} = 3R/2$ initially at 298 K and 10 L, is expanded, with the surroundings maintained at 298 K, to a final volume of 20 L, in three ways:
 (i) isothermally and reversibly,
 (ii) isothermally against a constant external pressure of 0.50 atm,
 (iii) adiabatically against a constant external pressure of 0.50 atm.

Calculate ΔS , ΔS_{SURR} , ΔH , ΔT , ΔA and ΔG for each path. If a numerical answer cannot be obtained from the data, write +, or -, or ? as appropriate.

- (l) Consider a perfect gas contained in a cylinder and separated by a frictionless adiabatic piston into two sections, A and B; Section B is in contact with a water bath that maintains it at constant temperature. Initially $T_A = T_B = 300 \text{ K}$, $V_A = V_B = 2.00 \text{ L}$, and $n_A = n_B = 2.00 \text{ mol}$. Heat is supplied to Section A and the piston moves to the right reversibly until the final volume of Section B is 1.00 L. Calculate: (i) the work done by the gas in Section A, (ii) ΔU for the gas in Section B, (iii) q for the gas in B, (iv) ΔU for the gas in A, and (v) q for the gas in A. Also calculate, (vi) ΔS_A and

3. (a) (i) Use the values of $\Delta_r G^0$ and $\Delta_r H^0$ at 298K to calculate $\Delta_r G^0(375\text{K})$ for the reaction:
 $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$
 (ii) Use the values of $\Delta_r G^0$ and $\Delta_r H^0$ at 298K to calculate $\Delta_r G^0(500\text{K})$ and $\Delta_r G^0(1000\text{K})$ for the reaction:
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
- (b) At 298K, the standard enthalpy of combustion of sucrose is $-5645 \text{ kJ mol}^{-1}$ and the standard Gibbs energy of the reaction is $-6333 \text{ kJ mol}^{-1}$. How much more non-expansion work may be obtained from this reaction if this reaction was to be carried at blood temperature, i.e. 37°C ?

- (c) Given the thermodynamic data for the sublimation of nitric acid hydrates at 220K:



where:

n	1	2	3
$\Delta_r G^0$ (kJ mol ⁻¹)	46.2	69.4	93.2
$\Delta_r H^0$ (kJ mol ⁻¹)	127	188	237

calculate $\Delta_r G^0(190\text{K})$. (State any assumptions made.)

4. (i) Derive an expression for the standard reaction Gibbs energy at a temperature T' in terms of its value at another temperature T and the coefficients a , b , c in the expression of molar heat capacity at constant pressure given by:

$$C_{p,m} = a + bT + \frac{c}{T^2}$$

- (ii) Use the values for a , b , and c as quoted in your data section of your textbook to evaluate the standard Gibbs energy of formation of liquid water at 372K from its value at 298K.