UNIVERSITY OF MALTA

DEPARTMENT OF CHEMISTRY

CH237 - Chemical Thermodynamics and Kinetics

Tutorial Sheet 7

1. (a) (i) The equilibrium constant for the isomerization of *cis*-2-butene to *trans*-2-butene is $K = 2.07$ at 400K. Calculate the standard reaction Gibbs energy.

    (ii) The standard reaction Gibbs energy of the isomerization of *cis*-2-pentene to *trans*-2-pentene at 400K is -3.67 kJmol^{-1}. Calculate the equilibrium constant of the isomerization.

    (b) (i) At 2257K and 1.00 atm total pressure, water is 1.77 percent dissociated at equilibrium by way of the reaction $H_2O(g) \rightleftharpoons H_2(g) + O_2(g)$. Calculate (a) K, (b) $\Delta_r G^0$, and (c) $\Delta_r G$ at this temperature.

    (ii) Dinitrogen tetroxide is 18.46 per cent dissociated at 25°C and 1 00 bar in the equilibrium $N_2O_4(g) \rightleftharpoons NO_2(g)$. Calculate (a) K, (b) $\Delta_r G^0$, and (c) K at 100°C given that $\Delta_r H^0 = +57.2$ kJmol^{-1} over the temperature range.

    (iii) Calculate the standard Gibbs energy and the equilibrium constant at (a) 298 K and (b) 400 K for the reaction $PbO(g) + CO(g) \rightleftharpoons Pb(s) + CO_2(g)$. (Note: You will need to make use of data from the 'Data Section' of your textbook.)

    (c) In the gas-phase reaction $2A + B \rightleftharpoons 3C + 2D$, it was found that, when 1.00 mol A, 2.00 mol B, and 1.00 mol D were mixed and allowed to come to equilibrium at 25°C, the resulting mixture contained 0.90 mol C at a total pressure of 1.00 bar. Calculate (i) the mole fractions of each species at equilibrium, (ii) K_x, (iii) K and (iv) $\Delta_r G^0$.

    (d) (i) The standard reaction enthalpy of $Zn(s) + H_2O(g) \rightleftharpoons ZnO(s) + H_2(g)$ is approximately constant at +224 kJmol^{-1} from 920K up to 1280K. The standard reaction Gibbs energy is +33 kJmol^{-1} at 1280K. Estimate the temperature at which the equilibrium constant becomes greater than 1.

    (ii) The standard enthalpy of a certain reaction is approximately constant at +125 kJmol^{-1} from 800K up to 1500K. The standard reaction Gibbs energy is +22 kJmol^{-1} at 1120K. Estimate the temperature at which the equilibrium constant becomes greater than 1.

    (e) The standard reaction Gibbs energy of the isomerization of borneol (C$_7$H$_{17}$OH) to isoborneol in the gas phase at 503K is +9.4kJmol^{-1}. Calculate the reaction Gibbs energy in a mixture consisting of 0.15 mol of borneol and 0.30 mol of isoborneol when the total pressure is 600 Torr.

    (f) (i) Use the data in your data section of your textbook to decide which of the following reactions have $K > 1$ at 298 K:

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(a) $HCl(g) + NH_3(g) \rightleftharpoons NH_4Cl(s)$

(b) $2Al_2O_3(s) + 3Si(s) \rightleftharpoons 3SiO_2(s) + 4Al(s)$

(c) $Fe(s) + H_2S(g) \rightleftharpoons FeS(s) + H_2(g)$

(d) $FeS(s) + H_2(g) \rightleftharpoons Fe(s) + H_2S(g)$

(e) $2H_2O_2(l) + H_2S(g) \rightleftharpoons FeS(s) + H_2(g)$

(ii) Which of these equilibria are favoured (in the sense of K increasing) by a reduction in temperature at constant pressure?

(g)   What is the standard enthalpy of a reaction for which the equilibrium constant is (i) doubled, (ii) halved when the temperature is increased by 10K at 298K?

(h)   The standard Gibbs energy of formation of $NH_3(g)$ is 16.5 kJmol^{-1} at 298K. What is the reaction Gibbs energy when the partial pressures of the N_2, H_2, and NH_3 (treated as perfect gases) are 3.0 bar, 1.0 bar, and 4.0 bar, respectively? What is the spontaneous direction of the reaction in this case?

(i)   The dissociation vapour pressure of NH_4Cl at 427°C 608 kPa but at 459°C it has risen to 1115 kPa. Calculate:
       (i) equilibrium constant at 427 °C,
       (ii) the standard reaction Gibbs energy at 427 °C,
       (iii) standard enthalpy at 427 °C,
       (iv) the standard entropy of dissociation at 427 °C.
(*NOTE:* Assume that the vapour behaves as a perfect gas and that $\Delta_r H^0$ and $\Delta_r S^0$ are independent of temperature in the range given.)

(j)   Estimate the temperature when:
       (i) $CaCO_3$ (calcite) decompises;
       (ii) $CuSO_4.5H_2O$ undergoes dehydration.
(*Note: You may need to make use of additional data from the data section in your textbook.*)

(k)   (i) At the half-way point in the titration of a weak acid wit strong base the pH was measured as 5.40.
       (a) What is the acidity constant and the pK_a of the acid?
       (b) What is the pH of the solution that is 0.015 M in the acid?

(ii) Calculate the pH of:
       (a) 0.10 M NH_4Cl (aq);
       (b) 0.10 M $NaCH_3CO_2$(aq);
       (c) 0.10 M CH_3COOH(aq).

(iii) Calculate the pH at the stoichiometric point of the titration of 25.00 mL of 0.100 M lactic acid with 0.175 M NaOH(aq).

(iv) Sketch the pH curve of a solution contains 0.10 M $NaCH_3CO_2$(aq) and a variable amount of acetic acid.

(v) Use information from your textbook (Table 9.1) to select suitable buffer for:
       (a) pH = 2.2, and
       (b) pH = 7.0.

(l) The equilibrium constant for the reaction, $I_2(s) + Br_2 \Leftrightarrow 2IBr(g)$ is 0.164 at 25°C.

(i) Calculate $\Delta_r G^0$ for this reaction.
(ii) Bromine gas is introduced into a container with excess solid iodine. The pressure and temperature are held at 0.164 atm and 25°C. Find the partial pressure of IBr(g) at equilibrium. (Assume that all the bromine is in the liquid form and that the vapour pressure of iodine is negligible.)
(iii) In fact, solid iodine has a measurable vapour pressure at 25 °C. In this case, how would the calculation have to be modified?

(m) The degree of dissociation, α_e, of $CO_2(g)$ into CO(g) and $O_2(g)$ at high temperatures was found to vary with temperature as follows:

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T/K          1395    1443    1498
αₑ/10⁻⁴      1.44    2.50    4.71
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calculate $\Delta_r H^0$ in this temperature range and K, $\Delta_r G^0$, and $\Delta_r S^0$ at each of these three temperatures. State the assumptions made (Note: You can make any justifiable approximation. In particular, assume $\Delta_r H^0$ to be constant over this temperature range.)

(n) Calculate the equilibrium constant of the reaction $CO(g) + H_2(g) \rightleftharpoons H_2CO(g)$ given that, for the production of liquid formaldehyde, $\Delta_r G^0 = +28.95$ kJmol^{-1} at 298 K and that the vapour pressure of formaldehyde is 1500 Torr at that temperature.

(o) Express the equilibrium constant of a gas-phase reaction A+3B = 2C in terms of the equilibrium value of the extent of reaction, ξ, given that initially A and B were present in stoichiometric proportions. Find an expression for ξ as a function of the total pressure, p, of the reaction mixture and sketch a graph of the expression obtained.

(p) Given the Ellingham diagram in your notes, discuss the thermodynamics of metal extraction from their oxides.