Tutorial 1 (not important for 2015)

1st Law of thermodynamics and other basic concepts Do No. 5 (*05-03-2015*)

1. One mole of an ideal gas is allowed to expand against a piston which supports 41 atm pressures. The temperature being constant at 0°C. The initial pressure was 1013.25 atm. Calculate w, q, ΔH and ΔU.

   (Problems on physical chemistry, ***S. Pahari, D. Pahari,*** Edition 1, chapter 5, Page 98)

2. 2 mole of an ideal gas undergoes isothermal and reversible expansion at 1096 K from 2 lit to 20 lit. Calculate the work done.

   (Problems on physical chemistry, ***S. Pahari, D. Pahari,*** Edition 1, chapter 5, Page 100)

3. 4 mole of an ideal gas undergoes isothermal and reversible expansion from v_1 to $10v_1$ lit. The initial pressure is 100 atm. Calculate the initial volume and temperature. If the work done by the system is 40 Kcal.

   (Problems on physical chemistry, ***S. Pahari, D. Pahari,*** Edition 1, chapter 5, Page 105)

4. Given the following heat of reaction at 25°C.
   $C_2H_4(g) + 3O_2(g) = 2CO_2(g) + 2H_2O(l)$ $\Delta H = -337.3$ Kcal

   $2H_2O(g) + O_2(g) = 2H_2O(l)$ $\Delta H = -136.6$ Kcal

   $2C_2H_6(g) + 7O_2(g) = 4CO_2(g) + 6H_2O(l)$ $\Delta H = -745.6$ Kcal

   Calculate the ΔH for following reaction.

   $C_2H_4(g) + H_2(g) = C_2H_6(g)$ at 25°C.

   (Problems on physical chemistry, ***S. Pahari, D. Pahari,*** Edition 1, chapter 5, Page 109)

5. A piece of zinc of mass 5.0 g is dropped into a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1.1 atm and the temperature 23°C.

   (Physical Chemistry, ***Atkins, P.W.; Paula, J. D.,*** 8th ed.; Chapter 2, pp 71, Problem No: 2.7b)

6. The value of $\Delta H°$ for the reaction $CO(g) + 0.5\ O_2(g) \rightarrow CO_2(g)$ is -282.97 kJ mol^{-1} at 298 K. Calculate $\Delta U°$ for the reaction.

   (Physical Chemistry, ***Laidler*****, K.J.;** ***Meiser***, J.H., 2nd ed; Chapter 2, pp 85, Problem No: 2.29**)**

7. A cylinder with a capacity of 22.4 *L* is filled with 1.00 *mol* of an ideal gas at 273.15 *K*. The gas is compressed irreversibly and isothermally (until $P = 1.50 \times 10^5\ Pa$) by increasing external pressure to $P = 1.50 \times 10^5\ Pa$. Find maximum and minimum amount of work done.

   (Text book of Physical chemistry, ***Robert G. Mortimer,*** Edition 3, Chapter 2, page 47, example 2.6)

8. CH_4 has standard state of enthalpy change of combustion of -890 $KJ\ mol^{-1}$ at 298.15 *K*. By using the standard enthalpy changes of H_2O (*l*) and CO_2 (*g*), find the enthalpy change of formation of methane.

   (Text book of Physical chemistry, ***Robert G. Mortimer,*** Edition 3, Chapter 2, page 89, example 2.30)

9. At constant temperature of -15 °*C* and constant pressure of 1.000 *atm*, super cooled liquid water (2.00 *mol*) freezes irreversibly. Find ΔH and q by assuming $C_{p,m}$ of liquid water and ice are 75.48 $KJ\ mol^{-1}$ and 37.15 $KJ\ mol^{-1}$ respectively and are constant.

   (Text book of Physical chemistry, ***Robert G. Mortimer,*** Edition 3, Chapter 2, page 70, example 2.20)

10. "Santa ana" winds originate from Californian Mountains at 0.81 *atm* pressure and 25 °*C* temperature (roughly 6000 *feet* above sea level) and are adiabatically and reversibly compressed as it moves to near sea level to a pressure of 1.00 *atm*. By assuming $C_{V,m} = 5R/2$ and ignoring temperature rise as effect of friction of air with ground, find the final temperature.

    (Text book of Physical chemistry, ***Robert G. Mortimer,*** Edition 3, Chapter 2, page 70, example 2.20)

Look at the previous years lecture notes for equations, if you do not understand.

Tutorial 2

Phase Equilibria, 2nd law,chemical equilibria Do All

11. Chloroform boils at 61.7 °*C*. Applying trouton's rule, estimate the vapor pressure of $CHCl_3$ at 50 °*C*.
    (Text book of Physical chemistry, ***Robert G. Mortimer,*** Edition 3, Chapter 5, page 212, example 5.6)

12. $CaCO_3\ (s) \rightleftharpoons CaO(s) + CO_2(g)$
    By using equilibrium constant quotient (K) and $\Delta_f G°$ values for the above reaction, estimate its equlibrium constant (K_a) and P_{eq} (CO_2) at 298.15 *K*.

[$\Delta_f G°$ (CO_2) = −394.389 *KJ mol*$^{-1}$; $\Delta_f G°$ (CaO) = −603.501 *KJ mol*$^{-1}$; $\Delta_f G°$ ($CaCO_3$) = −1128.79 *KJ mol*$^{-1}$]

(Text book of Physical chemistry, ***Robert G. Mortimer,*** Edition 3, Chapter 7, page 312, example 7.4)

13. Show that the change
    2 mol of an ideal gas (2 bar, 273 K) ⟶ 2 mol of gas (1 bar, 273 K) carried out irreversibly against an external pressure of 1 bar is spontaneous.

    (Text book of Physical chemistry, ***K. L Kapoor,*** Edition 3, *Vol 2,* Chapter 5, page 306, example 2)

14. A 50 g mass of Cu at a temperature of 393 K is placed in contact with 100 g mass of copper at a temperature of 303 K in a thermally insulated container. Calculate q and ΔS_{total} for the reversible process. Use a value of 0.4184 $Jg^{-1}K^{-1}$ for the specific heat capacity of Cu.

    (Text book of Physical chemistry, ***K. L Kapoor,*** Edition 3, *Vol 2,* Chapter 4, page 161, example 4)

15. Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when the volume of a sample of argon gas of mass 21 g at 298 K and 1.50 bar increases from 1.20 dm3 to 4.60 dm3 in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against p_{ex} = 0, and (c) an adiabatic reversible expansion.

    (Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 3, pp 113, Problem No: 3.13b)

16. A certain heat engine operates between 1000 K and 500 K. (a) What is the maximum efficiency of the engine? (b) Calculate the maximum work that can be done by for each 1.0 kJ of heat supplied by the hot source. (c) How much heat is discharged into the cold sink in a reversible process for each 1.0 kJ supplied by the hot source?

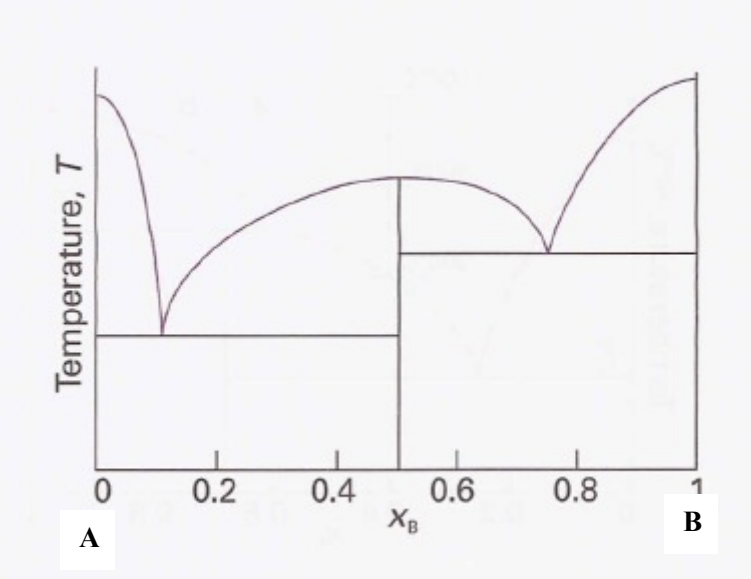
    (Physical Chemistry, ***Atkins, P.W.; Paula, J. D***. 8th ed.; Oxford: New York, 2006; Chapter 3, pp 114, Problem No: 3.15b)

17. What is the change in the boiling point of water at a 100^0C per Pascal change in atmospheric pressure?
    The Molar enthalpy of vaporization is 40.69 kJ mol^{-1}, the molar volume of liquid water is 0.019 × 10^{-3} m^3 mol^{-1}, and the molar volume of steam is 30.199 × 10^{-3} m^3 mol^{-1}, all at 100^0C and 1.01325 bar

    (Physical Chemistry, ***Silbey, Alberty, Bawendi***. Fourth Edition; Wiley India, Chapter 6, pp 182, example 6.1)

18. Label the regions of the phase diagram given below. State what substances (if compounds give their formnlas) exist in each region. Label each substance in each region as solid, liquid, or gas.

(Physical Chemistry, ***Atkins, P.W.; Paula, J. D***. 8th ed.; Oxford: New York, 2006; Chapter 6, pp 195, problem 6.6)



Tutorial 3

Elementary kinetics & Stat. Thermodynamics Do All

19. Consider the reaction $H_2 + Br_2 \longrightarrow 2HBr$. The reaction is carried out in a 0.25 L reaction vessel. The change in the amount of Br_2 in 0.01 s is -0.001 mol. A) What is the rate of conversion $d\xi/dt$? B) What is the rate of the reaction v? C) What are the values of $d[H_2]/dt$, $d[Br_2]/dt$, and $d[HBr]/dt$?
(Physical Chemistry, ***Silbey, R. J.; Alberty, R. A;Bawendi, M. G.***, 4th ed.; 2006; Chapter 18, pp 643, example 18.1)

20. At 400 K, the rate of decomposition of a gaseous compound initially at a pressure of 12.6 kPa, was 9.71 Pas^{-1} when 10.0 percent had reacted. It was 7.67 Pas^{-1} when 20.0 percent had reacted. What is the order of the reaction?
(Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 22, page 825, exercise 22.5b)

21. Radium has a half life of 1600 years. How much disintegration per sec would be undergone by 1 g of radium?

22. Specific rate of decomposition of a gas is given to be k = 2.80 x 10^{-3} dm^3 mol^{-1} s^{-1} at 30º C and 1.38 x 10^{-2} dm^3 mol^{-1} s^{-1} at 50º C. Calculate Arrhenius parameters for the reaction.
(Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 22, page 826, exercise 22.14a)

23. The activation energy of a first order reaction is 1,04,600 J mol^{-1} and pre exponential factor is 5 x 10^{13} s^{-1}. At what temperature will the reaction have a half-life of 30 days?

24. Consider a system A consisting of subsystems A_1 and A_2, for which $W_1 = 1 \times 10^{20}$ and $W_2 = 2 \times 10^{20}$. What is the number of configurations available to the combined system? Also compute the entropies S, S_1 and S_2.

(Atkins, P.W.; Paula, J. D. *Atkins' Physical Chemistry,* 8th ed.; Oxford: New York, 2006; Chapter 16, pp 586, Problem No: 16.1)

25. At what temperature would the population of the first excited rotational level of HCl be 1/e times its population of the ground state?

(Atkins, P.W.; Paula, J. D. *Atkins' Physical Chemistry,* 8th ed.; Oxford: New York, 2006; Chapter 16, pp 586, Problem No: 16.9b)

26. Consider a system of distinguishable particles having only three non-degenerate energy levels separated by an energy which is equal to the value of *k*T at 25 K. At 25 K calculate a) the ratio of populations in the states, b) the molecular partition function and c) the molar internal energy.

(Atkins, P.W.; Paula, J. D. *Atkins' Physical Chemistry,* 8th ed.; Oxford: New York, 2006; Chapter 16, pp 586, Problem No: 16.8b)

27. A certain molecule has a doubly degenerate excited state lying at 360 cm^{-1} above the non-degenerate ground state. At what temperature will 15 % of molecules be in upper state?

(Atkins, P.W.; Paula, J. D. *Atkins' Physical Chemistry,* 8th ed.; Oxford: New York, 2006; Chapter 16, pp 586, Problem No: 16.6b)

Tutorial 4

Kinectics of complex rxns, Reaction rate theories & Surface chemistry

Do All

28. The proposed mechanism for the reaction for the decomposition of N_2O_5 is as given below. Experimentally, the rate was found out as rate= k $[N_2O_5]$. Account for the rate law.

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$, $\upsilon = k [N_2O_5]$

(1) $N_2O_5 \rightleftharpoons NO_2 + NO_3$ k_1, k'_1

(2) $NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$ k_2

(3) $NO + N_2O_5 \rightarrow NO_2 + NO_2 + NO_2$ k_3

(Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 23, page 863, Problem No: 23.1b)

29. Consider the following chain mechanism:

(1) $A_2 \longrightarrow A^{\bullet} + A^{\bullet}$

(2) $A^{\bullet} \longrightarrow B + C$

(3) $A^{\bullet} + P \longrightarrow B^{\bullet}$

(4) $A^{\bullet} + B^{\bullet} \longrightarrow P$

Use the steady state approximation to deduce that the rate law for the consumption of A_2.

(Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 23, page 864, Problem No: 23.5b)

30. Calculate the collision frequency, z, and the collision density, Z, in carbon monoxide, R = 180 pm at 25^0C and 100 kPa. What is the percentage increase when the temperature is raised by 10 K at constant volume?

(Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 24, page 904, Problem No: 24.1b)

31. Calculate the magnitude of the diffusion-controlled rate constant at 298 K for a species in (a) decylbenzene, (b) concentrated sulfuric acid. The viscosities are 3.36 cP and 27 cP, respectively.

(Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 24, page 905, Problem No: 24.6b)

32. A rate constant is found to fit the expression $k_2 = (6.45 \times 10^{13}) \exp[-(5375\ K)/T]\ dm^3mol^{-1}s^{-1}$ near 25^0C. Calculate $\Delta^{\ddagger}G$ for the reaction at 25^0C.

(Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 24, page 905, Problem No: 24.11b)

33. Calculate the frequency of molecular collisions per square centimeter of surface in a vessel containing a) nitrogen b) methane at 25^0C when the pressure is (i) 10 Pa (ii) 0.150 μ Torr.

(Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 25, page 953, Problem No: 25.1b)

34. The adsorption of a gas is described by the Langmuir isotherm with K = 0.777 kPa-1 at 25^0C. Calculate the pressure at which the fractional surface coverage is (a) 0.20, (b) 0.75.

    (Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 25, page 953, Problem No: 25.8 b)

35. A certain solid sample adsorbs 0.63 mg of CO when the pressure of the gas is 36 kPa and the temperature is 300 K. The mass of gas adsorbed when the pressure is 4.0 kPa and the temperature is 300 K is 0.21 mg. The Langmuir isotherm is known to describe the adsorption. Find the fractional coverage of the surface at the two pressures.

    (Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 25, page 953, Problem No: 25.9 b)