

Explanations of the Exam and exercises in the course Principles in Physical Chemistry

The total mark is based on the Exam and exercises with weight of 75 % for Exam and 25 % for exercises.

The threshold to pass the course is 49 %. This is based on combined points. The threshold for 5 is 89 %

The exercise has different weight for each individual Chapter exercise. This is due to the fact that some of the exercises was more demanding than others. This makes it a bit complicated to compare the different exercise. There was one low weight exercise (Chapter 3) and I upscale it by factor 1.5. I also tested that each Chapter exercise had the same weight. This did change few marks but did not affect anyone to pass the course. I hope you can see the exercise points table in the Pearson page.

All the points with student numbers are in the MyCourses page.

Below are required facts of the exam answers: Each question except 3 has max of 6 points (3 have max of 5 p.) The total points is 35 p.

1. Table salt NaCl(s) dissolves quite easily to water, $\text{NaCl}(s) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$. What is the enthalpy and Gibbs energy change of this reaction in standard conditions? Explain what you compute. Is the reaction spontaneous? Repeat the calculations for KCl(s). Do KCl behave similarly as NaCl?

Explain how to compute the reaction Enthalpy : $\Delta H = \sum H(\text{products}) - \sum H(\text{reactants})$ (2 p explain both for H and G)

Use the data from Table 4.1, use ΔH_f of NaCl(s), Na⁺(aq), Cl⁻(aq) and KCl(s), K⁺(aq) (2 p needs correct data and correct answers)

Reaction Gibbs energy in the same manner: $\Delta G = \sum G(\text{products}) - \sum G(\text{reactants})$

here use ΔG_f from table 4.1.

The reaction is spontaneous if $\Delta G(\text{reaction})$ is negative (1 p)

KCl behave similarly as NaCl (1 p)

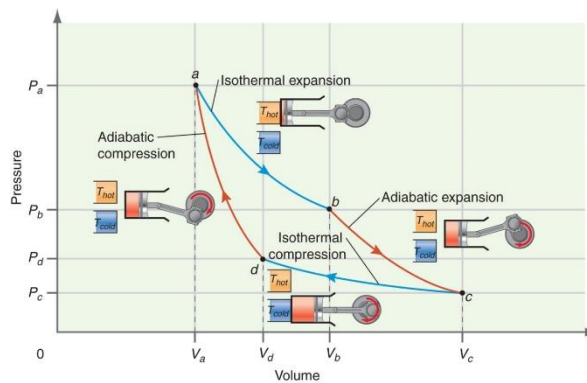
2. Explain the ideal heat engine cycle (or Carnot machine). What is the efficiency of this cycle. What is the efficiency of Loviisa nuclear plant when the steam temperature is 260-295 °C and the seawater with temperature of 10 °C is used for cooling. Compare that to the efficiency of a diesel engine with combustion temperature of 900 K and cooling 370 K.

Explain the figure 5.13. what type of process there are (4 steps). What are the heat and work in these steps (2 p.)

What is the total work done (1 p) and where the heat is transferred (1 p). What the efficiency means. Answ: the total work done divided by the total heat transfer w/q

See also Table 5.1

The numerical examples and conclusions (2 p.) Note that Kelvins should be used. $eff = 1 - T(cold)/T(hot)$



3.) The van der Waals equation of state parameters for O_2 are $a=1.38 \text{ dm}^6 \text{ bar/mol}$ and $b=0.0319 \text{ dm}^3/\text{mol}$. Explain what the vdW equation describes and to what phenomena the parameters or equation terms are linked. What is the compression factor? The compression factor is a bit difficult to compute. Why? You can estimate it by computing the $P_{vdw}(V_{id})/P_{id}$, where the V_{id} and P_{id} are the ideal gas molar volume and pressure. Do this comparison at 200, 300 and 400 K and at pressures of 50, 100, 150 bar. Comment the ideality of O_2 . Compare your numbers to the values of compressibility below.

Van der Waals Is an improvements to the ideal gas. (1 p) It will take into account the finite volume of the gas molecules (parameter b) and molecules attractive interactions (parameter b) (2 p.)

$$P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$

n can be set to = 1. then the eq is for 1 mol and the volume is the molar volume

compression factor $z = \frac{V_m}{V_m^{ideal}}$ is the ratio of real volume divided by the ideal gas volume. (1 p.)

The V(P,T) from vdW equation is complicate to compute because it is a 3'th order polyneme. The idea was to solve the $V_{id} = RT/P$ (n=1) and put that to the vdW equation and compare the P_{vdw}/P . I did this with excel so the computations did not take long. (1 p.)

You should compare these compression type values and make some conclusions. When $z < 1$ the gas is denser than the ideal gas, the attractive part dominates. and when $z > 1$ the repulsive part dominate and this happen at high temperatures. (1 p.) One could also take the values from the table in the question and explain the trends.

The end of problem did not go very well and I rescale this to 5 p. Some persons got still 6 p. Good for them.

4. What is the reaction Gibbs energy in standard conditions and how you can compute it for a general reaction. How the reaction Gibbs energy is related to equilibrium coefficient. How you can estimate the Gibbs energy at other temperatures than room temperature.

Reaction Gibbs energy standard conditions in the same manner as in problem 1: $\Delta G^\circ = \sum G^\circ(\text{products}) - \sum G^\circ(\text{reactants})$ and use data from some table like table 4.1. (1 p.)

In equilibrium the pressures are NOT = 1 atm so the pressure dependence need to take into account (see Chapter 6.7. and the log term below) and the reaction Gibbs energy = 0. (2 p.)

$$\Delta G_R = \Delta G_R^\circ + RT \ln \frac{P_B^\beta P_A^{-\alpha}}{P_o^{\beta-\alpha}} = \Delta G_R^\circ + RT \ln Q_P = 0$$

At equilibrium $Q = K$ or the equilibrium constant. This equation will define the equilibrium constant and it is important to understand the difference of ΔG° and ΔG (1 p.)

$$K_p = \exp(-\Delta G_R^\circ / RT), \text{ in case of two components } A \leftrightarrow B, K_p = P_A/P_B \text{ (or } K = \frac{[A]}{[B]}) \text{ (1 p.)}$$

The temperature dependence of G can be compute from (H is assumed to be constant)

$$\frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H(T_1) \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

I also accept the usage of $G = H - TS$ and explanation that the H and S do not change much (Chapter 6.9) Here the T_1 is room temperature (1 p.)

$$G(T_2) = H(T_1) - T_2 S(T_1)$$

4. Below is the phase diagram of Sulphur (Figure 1). Explain the phase changes at 1 atm and at 4.5×10^{-6} atm pressure when the system is heated. Does the system have a solid-liquid-gas triple point and if it have one where it is? Does the system have other triple points? What can you say of the molar volumes differences of the liquid and solid phases. Comment of both solid phases. Which, the Rhombic or Monoclinic phase, have larger molar volume.

Explanation at 1 atm (1p.) and 4.5×10^{-6} atm (1 p.). I would have hoped that the phase co-exist would have been mentioned. It was in some answers.

Triple points -solid-liq-gas (1 p.) the two other ones (1 p.)

The molar volumes. The molar volume can be concludes from the slope of the co-exist line if it is positive the phase above the line has the smaller molar volume. I also accept the reasoning that when the pressure increases (at constant temp) and a phase transition occur, the new phase has smaller molar volume. I even accept the experimental densities but often the molar volumes order come out of blue without any explanations. This is not sufficient. (2 p.)

6. Use a simple reaction $A \leftrightarrow I \leftrightarrow P$ as an example and explain what are the reaction rates and reaction constants and write the reaction equations. What are first and second order reactions. How you know the reaction order. If we assume that the $I \rightarrow P$ reaction is very slow what is the equilibrium constant of A and I and how it is related to the reaction constants?

The reaction rate is the speed of the reaction proceeds. The stoichiometric coefficient needs to be taken into account $Rate = \frac{d\xi}{dt} = \frac{1}{\nu} \frac{dn}{dt}$ (1 p.)

Reaction equation (for reaction $A + B \rightleftharpoons C + D$) $Rate = k f(A,B)$ and this is often in form $k [A]^a [B]^b$

here the k is the reaction constant. a and b are the reaction orders, typically 1 or 2. The reaction order need to be determined experimentally. (2 p.)

The reaction equations (2 p.)

$$\begin{aligned}\frac{d[A]}{dt} &= -k_{fA}[A] + k_{bA}[I], \\ \frac{d[I]}{dt} &= k_{fA}[A] - k_{bA}[I] - k_{fI}[I] + k_{bI}[P], \\ \frac{d[P]}{dt} &= k_{fI}[I] - k_{bI}[P]\end{aligned}$$

The equilibrium coefficient of A and I is $K = [I]/[A]$ (1 p.)

in equilibrium $\frac{d[A]}{dt} = 0$ so $k_{fA}[A] = k_{bA}[I] \Rightarrow \frac{[I]}{[A]} = \frac{k_{fA}}{k_{bA}}$ we do not need the information that the $I \rightarrow P$ reaction is slow but it is mentioned that people could concentrate to the first equations.