

Explanations of the Exam at 22.12. 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 90 %

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 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 has max of 6 points. The max total points are 36 p.

===== Exam at 22.12.21 =====

1) Methane (CH_4), cyclohexane (C_6H_{12} , a model for gasoline) and coal (mostly graphite) can be used as fuels. Write the combustion reactions (reaction with O_2). What is the reaction enthalpy and Gibbs energy. Explain what you compute. Are these reactions spontaneous? Which produces most heat per CO_2 molecule. (You can equal heat with the enthalpy change.) Natural gas (mostly methane) is considered "ecologically" (or CO_2) friendly. Do you agree with this and why?

Reaction equations: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, $C_6H_{12} + 9O_2 \rightarrow 6CO_2 + 6H_2O$, $C(\text{graph}) + O_2 \rightarrow CO_2$ (1 p)

Explain how to compute the reaction Enthalpy: $\Delta H = \sum H(\text{products}) - \sum H(\text{reactants})$ (1 p explain both for H and G)

Use the data from Table 4.1 and 4.2, use ΔH_f of $CH_4(g)$, $C_6H_{12}(g)$, $C(\text{graph},s)$, $CO_2(g)$, $H_2O(g)$ and $O_2(g)$ (2 p needs correct data and correct answers) Some of you used liquid water values. In this reaction water is in gas phase but no points were reduced if liquid values were used. The real burning temp is higher than 25 but this would complicate the computations.

$\Delta H(\text{graph})=0$, $\Delta H(CH_4)=-74.6$ kJ/mol, $\Delta H(C_6H_{12})=-156.4$ kJ/mol, $\Delta H(CO_2)=-393.5$ kJ/mol, $\Delta H(H_2O)=-241.8$ kJ/mol, $\Delta H(O_2)=0$

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

here use ΔG_f from tables 4.1 and 4.2.

$\Delta G(\text{graph})=0$, $\Delta H(CH_4)=-50.5$ kJ/mol, $\Delta H(C_6H_{12})=+26.8$ kJ/mol, $\Delta H(CO_2)=-394.4$ kJ/mol, $\Delta H(H_2O)=-220.6$ kJ/mol, $\Delta H(O_2)=0$

The reaction is spontaneous if $\Delta G(\text{reaction})$ is negative, all these reactions are spontaneous. (1 p)

heat/ CO_2 molec: CH_4 : 802.5 kJ/mol, C_6H_{12} : 609.2 kJ/mol and coal 395.5 kJ/mol, Methane is the best. (1 p)

2) Explain how the constant pressure calorimeter works. What can you measure with it? Why? What is the reaction enthalpy if you dissolve 2.01 g $K_2SO_4(s)$ to 120 g of water and the calorimeter cools 0.30 K. The calorimeters heat capacity is 342 J/K and waters molar heat capacity is 75.3 J/(K mol). Explain what you compute. Compare this to the table value of the reaction. Is the reaction exo- or endothermic?

Calorimeter: a thermally isolated system that can be used for reaction energy or enthalpy measurement. At constant pressure the reaction heat = enthalpy. (2 p.)

compute the q and ΔH , $q = (n(H_2O) \cdot C_p(H_2O) + C_p(\text{calorimeter})) \cdot \Delta T = 253 \text{ J}$.

The reaction heat is distributed to water **and** the calorimeter.

$q = n(\text{salt}) \cdot \Delta H$, $n(\text{salt}) = 2.01 \text{ g} / 174.3 \text{ g/mol} = 0.01153 \dots \text{ mol}$

$\Delta H = 21.9 \text{ kJ/mol}$ (the computations 3 p.)

$\Delta H(\text{react}) = 2\Delta H(K^+(\text{aq})) + \Delta H(SO_4^{2-}(\text{aq})) - \Delta H(K_2SO_4)$

From table 4.2 $\Delta H = 22.9 \text{ kJ/mol}$ (1 p.)

good agreement

Note the heat capacity of the ions are not taken into account. This is OK at low concentrations.

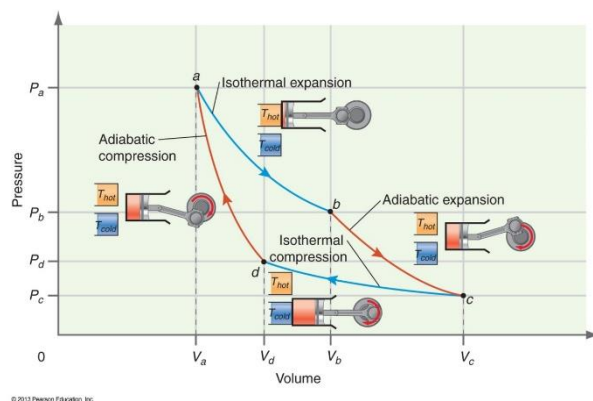
3) Explain the ideal heat engine cycle (or Carnot machine). How the heat and work flows in each step in the cycle. What is the efficiency of this cycle and why? What is the efficiency of Loviisa nuclear plant when the steam temperature is 260-295 °C and the seawater with temperature of 10 °C is used 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 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 (1 p.)

See also Table 5.1

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



4) The phase changes can be investigated using either P-T or P-V diagram (Figures 1 a) and b)) Explain how these two plot are connected by going in details the phase changes at constant pressure. It is easier to describe the changes by increasing the temperature. Choose a pressure where the solid-liquid and liquid-gas transitions occur. Explain what happens to volume in the process. Note that

letters a,b,c and lines in figures 1(a) and (b) do not correspond to the same process. Do not use water as an example.

A solid-liquid-gas evolution at constant pressure: (line b in left figure and line a in right fig). Pressure below the critical and above the triple points. (1 p)

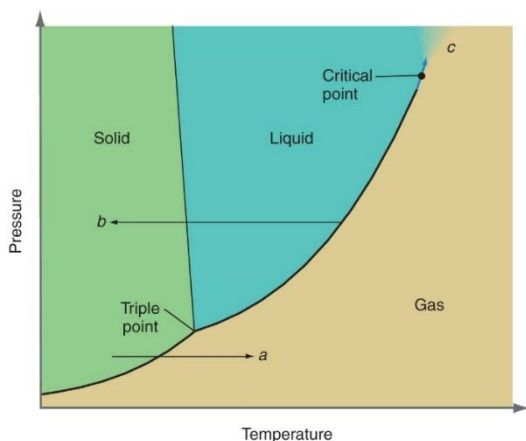
first solid, temp and volume increases (not required but bonus: $\Delta V = \alpha_s \Delta T$, α_s = solid thermal expansion coefficient) (1 p)

then solid-liquid transition at T_m (melting temp). At this temp the solid and liquid coexist and they have different volumes. The mixtures volume will change from $V(\text{solid})$ to $V(\text{liq})$. We assume that $V(\text{liq})$ is larger (2 p.)

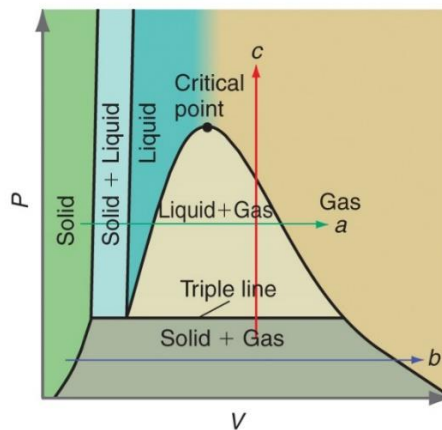
then liquid, T and V increases (not required but bonus: $\Delta V = \alpha_l \Delta T$, α_l = liquid thermal expansion coefficient) (0.5 p.)

then liquid-gas transition at T_b (boiling temp). At this temp the gas and liquid coexist and they have very different volumes. The mixtures volume will change from $V(\text{liq})$ to $V(\text{gas})$. The $V(\text{gas})$ is much larger (1 p.)

last the pure gas phase, here ideal gas can be used $PV = nRT$ or $V = \text{const } T$ (0.5 p.)



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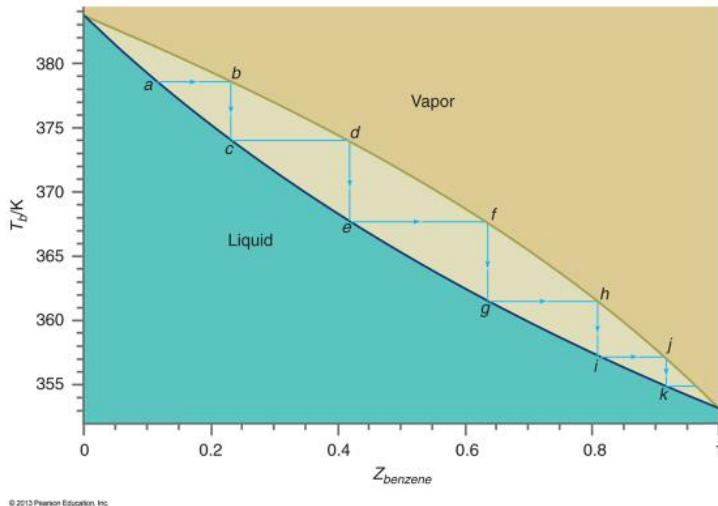
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5) Explain the fractional distillation process shown in figure 2. The components are benzene and toluene. You can assume that the solution mixture is ideal. What this means? Compute the vapor fractions for system with 5.0 mol of benzene and 2.5 mol of toluene. Explain why and how the fractional distillation procedure will lead to rather pure benzene.

For two components, vapor pressures $P^*(1)$ and $P^*(2)$, one has higher vapor pressure (in this case benzene). If the system is ideal the component 1 vapor pressure is $x(1)P^*(1)$ (and for component 2: $x(2)P^*(2)$), where the $x(1)$ the mole fraction in liquid. In gas phase the more volatile (with higher vapor pressure) have higher fraction = $x(1)P^*(1)/P(\text{tot})$. The total vapor pressure is $P(\text{tot}) = x(1)P^*(1) + x(2)P^*(2)$. The liquid and gas are in equilibrium (a and b, c and d, etc) (2 p.)

When the gas fraction is cooled to liquid (e.g. b to c) and it is then in equilibrium of vapor at d. The vapor d is again richer than liquid c. Repeating this we get to rather pure benzene. (2 p.)

The pure benzene vapor pressure at 25 C is 96.4 Torr and for toluene 28.9 Torr. The liquid mole fractions are 0.666 for benzene and 0.333 for toluene. The total pressure is 73.9 Torr and the vapor fractions are 0.87 for benzene and 0.13 for toluene. The gas is richer in benzene than the liquid. (2 p.)



6) NO react with hydrogen as $2H_2(g) + 2NO(g) \leftrightarrow N_2(g) + 2H_2O(g)$. 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? What is the reaction order and reaction constant of this reaction?

P(H ₂) (kPa)	P(NO) (kPa)	rate (kPa/s)
53.3	40.0	0.137
53.3	20.3	0.033
38.5	53.3	0.213
19.6	53.3	0.105

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 \leftrightarrow C + D) (this is a bit complicate since there is the backward reaction and nobody wrote these. I ignored this part)

$$\frac{d[H_2]}{dt} = -\frac{k_f}{2} [H_2]^a [NO]^b + \frac{k_b}{2} [N_2]^c [H_2O]^d,$$

Rate = k f(A,B) and this is often in form of k [A]^a[B]^b

or k[P(A)]^a[P(B)]^b where the k is the reaction rate constant. a and b are the reaction orders, typically 1 or 2. The reaction equation or orders need to determine experimentally.

We assume the form $\text{Rate} = k [\text{P(A)}]^a [\text{P(B)}]^b$ and $\text{A} = \text{H}_2$ and $\text{B} = \text{NO}$ (2 p.)

$\text{P(H}_2\text{)}$ is the same in lines 1 and 2 then (1p.)

$$\frac{R_1}{R_2} = \frac{k [A_1]^a [B_1]^b}{k [A_2]^a [B_2]^b} = \frac{k [A_1]^a [B_1]^b}{k [A_1]^a [B_2]^b} = \frac{[B_1]^b}{[B_2]^b} \Rightarrow \frac{0.137}{0.033} = \left(\frac{40.0}{20.3}\right)^b \Rightarrow 4.15 = (1.97)^b \Rightarrow$$
$$b = \frac{\ln(4.15)}{\ln(1.97)} = 2.1 \approx 2$$

P(NO) is same for lines 3 and 4 (1 p.)

$$\frac{R_3}{R_4} = \frac{k [A_3]^a [B_3]^2}{k [A_4]^a [B_3]^2} = \frac{[A_3]^a}{[A_4]^a} \Rightarrow \frac{0.213}{0.105} = \left(\frac{38.5}{19.6}\right)^a \Rightarrow 2.03 = (0.96)^a \Rightarrow a = 1$$

rate constant, note the units (1p.)

$$R_1 = k [A_1]^1 [B_1]^2 \Rightarrow k = \frac{0.137}{53.3 * (40.0)^2} \frac{1}{(\text{kPa})^2 \text{ s}} = \frac{1.6 * 10^{-6}}{(\text{kPa})^2 \text{ s}}$$

same results for reaction 2 and 3