

Explanations of the Exam (2.11) 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.

===== Exam at 2.11.21 =====

1. Cyclohexane (C₆H₁₂) and ethanol (C₂H₅OH) can be used as fuels. Write the combustion reactions (reaction with O₂). What is the reaction enthalpy and entropy. Explain what you compute. Are these reactions spontaneous? Which produces more heat per CO₂ molecule. (You can equal heat with the enthalpy change.) What is the maximum nonexpansion work per mole these fuels can do?

Reactions:

$C_6H_{12} + 9O_2 \rightarrow 6CO_2 + 6H_2O$ and $C_2H_5OH + 3.5 O_2 \rightarrow 2CO_2 + 3H_2O$ (There was a typo in ethanol equation C₂H₄OH so also $C_2H_4OH + 3.25 O_2 \rightarrow 2CO_2 + 2.5H_2O$ is OK but pretty ugly) (1 p)

Explain how to compute the reaction Enthalpy : $\Delta H = \sum H(\text{products}) - \sum H(\text{reactants})$

Reaction Gibbs energy in the same manner: $\Delta G = \sum G(\text{products}) - \sum G(\text{reactants})$ (1 p explain both for H and G)

Use the data from Table 4.2, use ΔH_f and ΔG_f of C₆H₁₂(l), C₂H₆O(l) CO₂(g), H₂O(g) (or H₂O(l)) (2 p needs correct data and correct answers)

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

The heat productions is similar (1 p)

The maximum nonexpansion work per mole these fuels is the $\Delta G(\text{reaction})$.

2. Explain how the constant pressure calorimeter works. What can you measure with it? What is the reaction enthalpy if you dissolve 1.423 g Na₂SO₄(s) to 80 g of water and the calorimeter heats 0.036

K. The calorimeters heat capacity is 342.5 J/K and water molar heat capacity is 75.3 J/(K mol). Compare this to the table value of the reaction.

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 , $q = (n(\text{H}_2\text{O}) \cdot C_p(\text{H}_2\text{O}) + C_p(\text{calorimeter})) \cdot \Delta T = 24.4 \text{ J}$.

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

$q = n(\text{salt}) \cdot \Delta H$, $n(\text{salt}) = 1.423 \text{ g} / 142.04 \text{ g/mol} = 0.010 \text{ mol}$

$\Delta H = 2.44 \text{ kJ/mol}$ (the computations 3 p.)

$\Delta H(\text{react}) = 2\Delta H(\text{Na}^+(\text{aq})) + \Delta H(\text{SO}_4^{2-}(\text{aq})) - \Delta H(\text{Na}_2\text{SO}_4)$

From table 4.2 $\Delta H = 2.4 \text{ kJ/mol}$ (1 p.)

good agreement

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

3. 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.)

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

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

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

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. 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 happen to volume when the temperature change. Note that letters a,b,c and lines in these figures are not connected. Line a in not the same process in figures a) and b). 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). below the critical and above the triple points. (1 p)

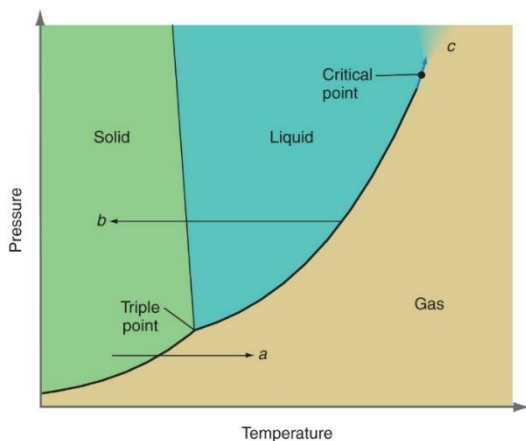
first solid, temp and volume increases (not required but bonus: $\Delta V = \alpha_s \Delta T$, α_s = solid thermal expansion coefficient) (1 p)

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.)

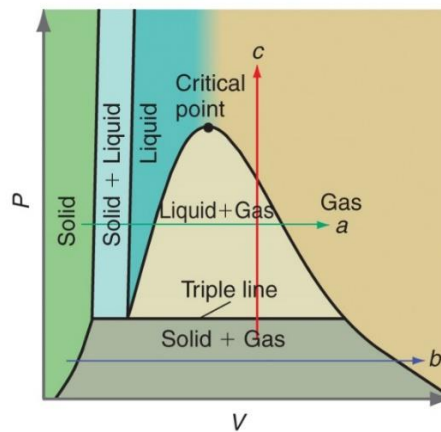
then liquid, T and V increases (not required but bonus: $\Delta V = \alpha_l \Delta T$, α_l = liquid thermal expansion coefficient) (1 p.)

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 (0.5 p.)

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



© 2013 Pearson Education, Inc.



© 2013 Pearson Education, Inc.

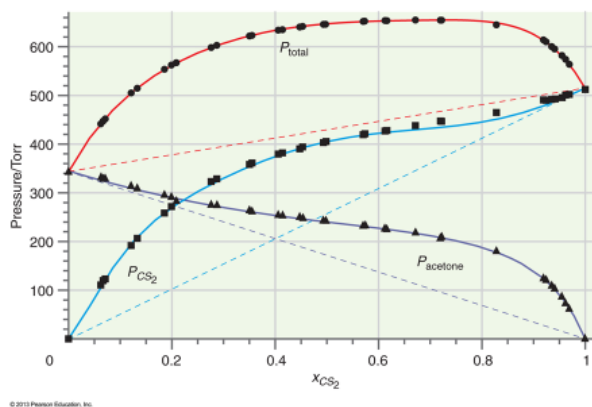
5) What are the partial pressures of mixture of two ideal liquids with respect of the concentration (at room temperature) if the partial pressures of pure liquids are P_1 and P_2 . The figure 2 shows the pressures of CS_2 -acetone mixture. Is this system ideal? What is the Henry's law? Explain both the CS_2 and acetone partial pressures at low and high CS_2 limits.

In ideal system the partial pressure is $P_1 = x_1 P_1(\text{pure})$, $P(\text{tot}) = x_1 P_1(\text{pure}) + x_2 P_2(\text{pure})$, $x_2 = 1 - x_1$, where x_i is the mole fraction of component i in the liquid. $P(\text{pure})$ is the pure liquid gas pressure (at normal cond) (2 p.)

The CS_2 -acetone system is not ideal. Neither of the partial pressures are linear. The total pressure is even less. (1 p.)

Henry's law, $P_1 = k_{H,1} x_1$, k is empirical (1 p.)

CS_2 and acetone partial pressures at low and high CS_2 limits: at low second component concentrations quite ideal, especially for acetone (see $P(\text{acetone})$ when $x(\text{CS}_2)$ small). At high second component concentrations systems are not ideal (far from the linear line). Here one should use Henry's law. (2 p.)



6. In atmosphere the ozone (O_3) can react with HO_2 radical. Below is a table with the concentration (in molec/cm³) and the rates. What are the reaction orders and rate constant of this reaction? Explain how you will do the calculations.

$[\text{HO}_2^*]$ (1/cm ³)	$[\text{O}_3]$ (1/cm ³)	rate (1/(s cm ³))
$1.0 \cdot 10^{11}$	$1.0 \cdot 10^{12}$	$1.9 \cdot 10^8$
$1.0 \cdot 10^{11}$	$5.0 \cdot 10^{12}$	$9.5 \cdot 10^8$
$3.0 \cdot 10^{11}$	$1.0 \cdot 10^{12}$	$5.7 \cdot 10^8$

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

Reaction equation (for reaction $\text{A} + \text{B} \leftrightarrow \text{C} + \text{D}$) $\text{Rate} = k f(\text{A}, \text{B})$ and this is often in form of $k [\text{A}]^a [\text{B}]^b$ where the k is the reaction rate constant. a and b are the reaction orders, typically 1 or 2

We assume the form $\text{Rate} = k [\text{A}]^a [\text{B}]^b$ and $\text{A} = \text{HO}_2$ (typo in text should be HO_2 not OH_2) and $\text{B} = \text{O}_3$ (3 p.)

$[\text{O}_3]$ is the same in lines 1 and 3 then (1p.)

$$\frac{R_1}{R_3} = \frac{k [\text{A}_1]^a [\text{B}_1]^b}{k [\text{A}_3]^a [\text{B}_3]^b} = \frac{k [\text{A}_1]^a [\text{B}_1]^b}{k [\text{A}_3]^a [\text{B}_1]^b} = \frac{[\text{A}_1]^a}{[\text{A}_3]^a} \Rightarrow \frac{1.9}{5.7} = \left(\frac{1.0}{3.0}\right)^a \Rightarrow \frac{1}{3} = \left(\frac{1}{3}\right)^1 \Rightarrow a = 1$$

$[\text{HO}_2]$ is same for 1 and 2 (1 p.)

$$\frac{R_1}{R_2} = \frac{k [A_1]^1 [B_1]^b}{k [A_1]^1 [B_2]^b} = \frac{[B_1]^b}{[B_2]^b} \Rightarrow \frac{1.9}{9.5} = \left(\frac{1.0}{5.0}\right)^b \Rightarrow \frac{1}{5} = \left(\frac{1}{5}\right)^1 \Rightarrow b = 1$$

rate const (1p.)

$$R_1 = k [A_1]^1 [B_1]^1 \Rightarrow k = \frac{1.9 * 10^8}{1.0 * 10^{11} * 1.0 * 10^{12}} \frac{cm^3}{s} = \frac{1.9 * 10^{-15} cm^3}{s}$$

same results for reaction 2 and 3