

### NAME

### SURNAME

				EXAM (60%)

**Important:** Please, write down your name. Read the exam carefully before you start. Write down the answers in the blank spaces provided right after each exercise. You may use the last page for drafts. Time available for the test is 2:30 h.

## 1. (1 mark, 10 min)

- Given the following molecules: (a)  $XeF_2$ ; (b)  $CO_2$ ; (c)  $OF_2$ ; (d)  $C_2H_4$ ; (e)  $NO_2^-$ ; (f)  $N_2H_4$ .
- Which of the following molecules would be linear? And planar?
- Which of the following molecules would be angular?
- Which have lone pairs around the central atom?
- Predict the hybridisation of carbon atoms in molecules (b) and (d)
- Which of the following molecules are polar?

**Data:** Atomic numbers (Z): H(Z=1); C(Z=6); N(Z=7); O(Z=8); F(Z=9); Xe(Z=54). The hydrazine (N<sub>2</sub>H<sub>4</sub>) has a dipole moment of 1.85 D.

2. (1 points, 10 mins) Consider a mixture of two volatile liquids A and B, where A is the most volatile liquid. Discuss whether the following statements are true or false and give a reason for your answer.

(a) The boiling temperature of the mixture only depends on the external pressure

(b) The boiling temperature of the mixture will be higher the higher the mole fraction of component A in the liquid mixture

(c) The boiling temperature of the mixture is will be lower than the boiling temperature of B ( $T_b^{0}(B)$ ) and higher than that of A ( $T_b^{0}(A)$ ).

(d) In a rectification column component A will be obtained at the bottom whereas component B will be obtained at the head of the distillation column.

(e) At the same temperature, vapour pressure of component A will be higher than vapour pressure of component B.

**3.** (1 points, 15 mins). Name the main factors that influence the rate of a chemical reaction. Please provide a brief explanation for each factor and how it affects the rate of a chemical reaction.

4. (1.5 points, 15 mins) The following electrochemical reactions take place in a lead acid battery as those commonly used in automobiles:

$$PbSO_{4} (s) + 2e^{-} \rightarrow Pb (s) + SO_{4}^{2-} \qquad E^{0} = -0.356 V$$
(s) + SO<sub>4</sub><sup>2-</sup> (aq) + 4H<sup>+</sup> (aq) + 2e<sup>-</sup>  $\rightarrow PbSO_{4} (s) + 2 H_{2}O (l) \qquad E^{0} = 1.685 V$ 

- a) Write down the overall cell reaction and calculate the standard cell potential
- b) How many elements are needed to get an output voltage of 12V as those used in the car batteries?
- c) If the anode is made with 4 kg of lead, how many moles of Pb are there? Calculate the total amount of charge (in Coulombs, C) that can be accumulated in the battery.
- d) Calculate Gibbs free energy of the battery and estimate the equilibrium constant of the battery (at equilibrium and for 25 °C).

**Data:**  $F = 96500 \text{ C} \cdot \text{mol}^{-1}$ ; M (Pb) = 207 g·mol^{-1}; R = 8.314 J·mol^{-1} \cdot \text{K}^{-1}.

PbO<sub>2</sub>

5. (1.5 points, 15 min) Octane is burnt in an engine with 20% excess air.

a) Write down the balanced combustion equation with air and calculate the heat under constant pressure conditions. Assume that water is obtained in the liquid state.

b) Is the engine working under rich or lean conditions? Discuss the advantages of working under these conditions.

c) Calculate the average molar mass of air. Then calculate the air to fuel ratio (in kg).

Assume air is formed mainly by oxygen and nitrogen in a ratio (21% O<sub>2</sub>; 79% N<sub>2</sub>).

**Data:**  $\Delta H_f \circ (C_8 H_{18}) = -248.5 \text{ kJ/mol}; \Delta H_f \circ (H_2 O, I) = -285.8 \text{ kJ/mol}; \Delta H_f \circ (CO_2) = -393.509 \text{ kJ/mol}; M(N_2) = 28 \text{ g/mol}; M(O_2) = 32 \text{ g/mol}; M(C_8 H_{18}) = 114.23 \text{ g/mol}; R = 0.082 \text{ atm} \cdot I \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ 

## 6. (1.5 marks, 15 mins)

1 mol of CO is added to a 2 L flask at 427 °C with a catalyst to produce the following reaction:

CO (g) + 2 H<sub>2</sub> (g) → CH<sub>3</sub>OH (g) 
$$\Delta H_{r}^{0} = -91.07 \text{ kJ} \cdot \text{mol}^{-1}$$

A certain amount of  $H_2$  is added, after reaching equilibrium, the total pressure is 60 atm. 0.0148 mol of methanol are formed. Calculate:

- a) Equilibrium constants given in terms of concentrations ( $K_c$ ) and in terms of partial pressures ( $K_p$ ) at 427°C.
- b)  $\Delta G^0_r$  and  $\Delta S^0_r$  at 427 °C.

After reaching equilibrium, temperature decreases to 25 °C, calculate:

c)  $\Delta G_r^0$  and the new equilibrium constant (K<sub>p</sub>) at 25°C. Is K<sub>p</sub> (at 25 °C) higher or lower than K<sub>p</sub> at 427 °C? Explain your answer.

**Note**:  $\Delta H_r^0$  and  $\Delta S_r^0$  do not vary during cooling, and all compounds remain in gas phase. **Data**: 8.314 J/g = 0.082 atm I mol<sup>-1</sup> K<sup>-1</sup>.

7. (1.0 marks, 15 mins) Indicate whether the following statements are true (T) or false (F).

# Correct answers +0.1p; Incorrect answers -0.05p.

	- 1	
	1	The hydrohalogenation reaction is an elimination reaction that usually yields as a product an alkene.
	2	The chlorination of alkanes proceeds as a radical substitution reaction that takes place in three
	2	different steps: initiation, propagation and termination.
		In the following reaction elimination and a redox processes takes place:
	3	
		$CH_3\text{-}CHBr\text{-}CHBr\text{-}CH_3 + Zn \rightarrow CH_3\text{-}CH=CH\text{-}CH_3 + ZnBr_2$
	4	Pyrogenation of coal is based on a thermal treatment with oxygen at high temperature to obtain
	4	liquid hydrocarbons.
	5	From methane it is possible to obtain syngas (CO + H <sub>2</sub> ) which is used as raw material for many
		industrial processes.
	6	In the combustion of a fuel, a <i>rich mixture</i> is a mixture with an excess of air.
	7	Obtaining methods of alkenes usually involve addition reactions.
	8	The quantity known as higher heating value (HHV) is determined by bringing all the products of
	ð	combustion back to the original temperature, usually to 25°C.
	9	Flash distillation is used mainly to obtain substances that are temperature sensitive materials
	10	In organic reactions, a heterolytic bond cleavage yields as a result two ionic compounds, the
		carbocation and a carbanion.

8. (1.5 points, 15 min) The final step in the fabrication process of nitric acid is a distillation in which the acid is concentrated from 60% to 99% (weight percentages in aqueous solutions). The presence of sulfuric acid, which is not fed or extracted to the system, decreases water partial pressure, thus it is possible to increase the concentration of nitric acid by distillation.

Using the flowchart given below and considering that a stream of 100 kg h<sup>-1</sup> of concentrated nitric acid of 99% leaves the system (B, stream) determine:

- a) The mass flow of sulfuric acid that is recirculated.
- b) Mass flow of dilute nitric acid in the feed stream.
- c) The efficiency of the overall process for the elimination of water.

NOTE: All percentages are in weight.

