Self-assessment test with focus on COSOM subjects (1) (solutions)

1. At given temperature $T_1$ a real gas has a certain volume $V_1$ and a certain pressure $p_1$. Upon isothermal compression the gas will start to liquefy until it is fully liquid at a volume of $0.2 V_1$. Calculate the mole fraction of the substance at a volume of $0.3 V_1$ in liquid phase and gas phase respectively.

Isothermal means $T$ is a constant throughout the whole process. Upon phase transition, $p$ is also a constant. At $V_1$ all substance is in its gaseous state making a molar fraction of 1 or 100 %. At $0.2 V_1$, when everything is liquefied, no more substance is in the gas phase making a molar fraction of 0 or 0 %. With these data points at hand, one can calculate the molar fraction of substance in the gas phase at $0.3 V_1$ by a simple linear equation:

$$y = \frac{1}{0.8 V_1} x - \frac{1}{4} = \frac{1}{0.8 V_1} \cdot 0.3 V_1 - \frac{1}{4} = \frac{3}{8} = 0.125 = 12.5 \%$$

This means that 87.5 % of substance is already in a liquid state.

2. The combustion enthalpy of ethanol ($C_2H_5OH$) is -1368 kJ/mol. During the combustion of ethanol under constant pressure in a calorimeter with a heat capacity of 7.3 kJ/K, an increase in temperature of $T = 1500$ K is measured. Calculate the mass of ethanol burned in this process. Notes: molar masses of C: 12.01 g/mol, H: 1.01 g/mol and O: 16.00 g/mol

The energy gained from the combustion of 1 mol ethanol is 1368 kJ. The calorimeter measured a temperature increase of 1500 K. Thus, the energy gain here is: $Q = C \Delta T = 7.3 \frac{kJ}{K} \cdot 1500 K = 10950 kJ$ which is about 8x more than 1368 kJ. Neglecting energy losses, 8 mols of ethanol were burned, which is around 369 g.

3. Condensed phases are the consequence of intermolecular forces.

a) What is the intermolecular force that allows us to liquefy noble gases?

London dispersion forces.

b) Which are the major quantities?

Polarizability, spontaneous dipole formation, dipole induction

c) How does the interaction potential $V(R)$ depend on the distance $R$ between the nuclei?

$$V(R) \sim \frac{C}{R^6}$$ with $C$ being a constant value
4. Consider a system consisting of one component. Upon increase of temperature at constant pressure, the system undergoes a phase transition from liquid to gaseous. Sketch the heat capacity \((c_V)\) curve as a function of temperature \((T)\). How does the magnitude change during phase transition and what value does \(c_V\) then take on?

Upon phase transition \(c_V\) goes up to an infinite value. This is due to the definition of \(c_V\):

\[
c_V = \frac{\delta Q}{\delta T} |_V
\]

meaning at constant volume more heat energy transfers to an increase in temperature which is true except upon phase transition because here all energy pumped into the system is required to evaporate the liquid. Temperature doesn’t change (stays at 100 °C for water) until all liquid is evaporated.

5. Sketch the \((p, T)\) phase diagram of water.
   a) Mark all the present phases. What is the so-called “anomaly of water”?

Water has a melting curve with negative slope. Liquid water has a higher density than closely packed ice.

b) Can a phase diagram of a pure substance show more than one triple point? If so, please give an example.

Yes, if there are more than one modification in the solid state. Examples: sulfur, water.
6. How does the equilibrium constant $k$ depend on temperature? How can one measure this dependency?

$$k(T) = A \exp \left( -\frac{E_a}{k_B T} \right)$$

A is a constant, $E_a$ is the activation energy of a reaction and $k_B$ is Boltzmann’s constant. The higher the temperature, the more reactants have the necessary amount of energy to bypass the activation barrier in order to react with each other. By performing the same reaction at different temperatures while measuring the reaction velocity, one can observe a dependency of $k(T)$ by $T$. 