

Tutorials 2 Thermodynamics 2, 2023/2024

Exercise 5

Dichloromethane has a vapour pressure of 400 Torr at 24.1 °C and an enthalpy of vaporization of $\Delta_{\text{vap}}H = 28.7$ kJ/mol.

Estimate the temperature at which the vapour pressure equals 500 Torr. Assume that the vapour behaves as a perfect gas and that the enthalpy of vaporization is independent of the temperature in this pressure range.

Exercise 6

Mercury has an enthalpy of fusion of $\Delta_{\text{fus}}H = 2.292$ kJ/mol and a melting point (at 1 atm) of $T_{\text{fus}} = 234.3$ K. The volume change upon freezing is $\Delta_{\text{fus}}V = 0.517$ cm³/mol and the liquid has a density of $\rho(l) = 13.6$ g/cm³.

At what temperature will the bottom of a mercury column of 10.0 m freeze?

Hint: Start from the Clapeyron equation and use $\Delta_{\text{fus}}G = \Delta_{\text{fus}}H - T_{\text{fus}}\Delta_{\text{fus}}S = 0$ and realize that $\Delta_{\text{fus}}H$ and $\Delta_{\text{fus}}V$ will hardly change for the small temperature difference that you will find.

Exercise 7

Construct and sketch a phase diagram of benzene near its triple point (36 Torr and 5.50 °C).

Use the following data, $\Delta_{\text{fus}}H = 10.6$ kJ/mol, $\Delta_{\text{vap}}H = 30.8$ kJ/mol, $\rho(s) = 0.891$ g/cm³ and $\rho(l) = 0.879$ g/cm³.

Hint: use the Clapeyron equation for the three relevant phase transitions, and assume that ΔH and ΔV hardly change around the triple point.

Exercise 8

One mole of liquid (molar mass $M = 200$ g/mol, density $\rho = 2 \cdot 10^3$ g/l and a thermal expansion coefficient $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = 2 \cdot 10^{-3}$ K⁻¹) is isothermally pressurised from $P_1 = 1$ bar to $P_2 = 100$ bar at 27 °C. The volume change in this process is negligible.

Calculate the change in

- Entropy; use a Maxwell relation between S, P, V and T .
- Internal energy
- Enthalpy
- Helmholtz free energy
- Gibbs free energy

Exercise 9

The Clapeyron equation cannot be applied to a second order phase transition. For such a transition one can use the Ehrenfest equation (the two phases are labeled with 1 and 2):

$$\frac{dP}{dT} = \frac{\alpha_2 - \alpha_1}{\kappa_{T,2} - \kappa_{T,1}} \quad \text{and} \quad \frac{dP}{dT} = \frac{C_{P,m,2} - C_{P,m,1}}{TV_m(\alpha_2 - \alpha_1)},$$

in which α is the thermal expansion coefficient and κ_T the isothermal compressibility (cf. exercise 4).

- a) Why is the Clapeyron equation not applicable for a second order phase transition?
- b) Use the fact that S and V are continuous functions in a second order phase transition, to derive the Ehrenfest equation. To do this, write the total differentials of V and S as a function of T and P .
- Hint: use for the derivation of the second equation that at the phase boundary, so in an equilibrium situation

$$dS|_P = \frac{dQ^{rev}}{T}|_P = \frac{dH}{T}|_P = \frac{C_P dT}{T} \quad \text{so} \quad \left(\frac{\partial S_m}{\partial T} \right)_P = \frac{C_{P,m}}{T},$$

as well as a Maxwell relation.