

Answers Tutorials 2 Thermodynamics 2, 2023/2024

Exercise 5

We assume that the vapour behaves as a perfect gas, and that the enthalpy of vaporization is independent of the temperature in the pressure interval. With these assumptions the Clausius-Clapeyron equation becomes:

$$P = P^* \exp(-\chi) \quad \text{with} \quad \chi = \frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \quad \text{which implies}$$

$$\ln \frac{P^*}{P} = \chi,$$

or

$$\frac{1}{T} = \frac{1}{T^*} + \frac{R}{\Delta_{\text{vap}}H} \ln \frac{P^*}{P} = \frac{1}{297.25} + \left(\frac{8.314}{28.7 \cdot 10^3} \right) \ln \frac{400}{500} = 3.30 \cdot 10^{-3} \text{ K}^{-1},$$

so $T = 303 \text{ K} = 30 \text{ }^\circ\text{C}$.

Exercise 6

The change in freezing point as a result of the higher pressure in the mercury column can be calculated with the Clapeyron equation (use $\Delta_{\text{fus}}G = \Delta_{\text{fus}}H - T_{\text{fus}}\Delta_{\text{fus}}S = 0$ for a phase transition (so at $T = T_{\text{fus}}$)).

$$\frac{dP}{dT} = \frac{\Delta_{\text{fus}}S}{\Delta_{\text{fus}}V} = \frac{\Delta_{\text{fus}}H}{T_{\text{fus}}\Delta_{\text{fus}}V}, \quad \text{so} \quad dP = \frac{\Delta_{\text{fus}}H}{T_{\text{fus}}\Delta_{\text{fus}}V} dT \quad \text{and} \quad \int_{P_1}^{P_2} dP = \int_{T_{\text{fus}}}^{T_{\text{fus},2}} \frac{\Delta_{\text{fus}}H}{T_{\text{fus}}\Delta_{\text{fus}}V} dT.$$

The Clapeyron equation describes the pressure change as a function of the temperature as long as we stay on the phase boundary line, which means that we should actually write dP_{fus} and dT_{fus} instead of dP and dT . We assume that for the small temperature change all quantities in the integral (except for T_{fus} which changes due to the pressure in the mercury column) are constant, which leads to

$$P_2 - P_1 = \frac{\Delta_{\text{fus}}H}{\Delta_{\text{fus}}V} \int_{T_{\text{fus}}}^{T_{\text{fus},2}} \frac{dT}{T} = \frac{\Delta_{\text{fus}}H}{\Delta_{\text{fus}}V} \ln \frac{T_{\text{fus},2}}{T_{\text{fus}}}.$$

The total pressure difference over the column is $(P_2 - P_1) = \rho(l)gh$, with h the column height and $g = 9.81 \text{ m/s}^2$, which results in a change in freezing point at the bottom of the column determined by

$$\ln \frac{T_{\text{fus},2}}{234.3} = (P_2 - P_1) \frac{\Delta_{\text{fus}}V}{\Delta_{\text{fus}}H} = \rho(l)gh \frac{\Delta_{\text{fus}}V}{\Delta_{\text{fus}}H} = 13.6 \cdot 10^3 \cdot 9.81 \cdot 10.0 \frac{0.517 \cdot 10^{-6}}{2.292 \cdot 10^3} = 3.0094 \cdot 10^{-4}.$$

This results in a temperature $T_{\text{fus},2} = 234.4 \text{ K}$, so an increase of 0.1 K .

The answer therefore is that the bottom of the column just freezes at a temperature of 234.4 K .

Exercise 7

The three phase boundary lines intersect in the triple point. These lines can be found using the following equations between P and T for the phase boundaries in a (P, T) -diagram. ((P, T) and (P^*, T^*) correspond to two points on a phase boundary line):

$$P = P^* + \frac{\Delta_{\text{fus}}H}{\Delta_{\text{fus}}V} \ln \frac{T}{T^*} \quad (\text{s-l}),$$

$$P = P^* \exp(-\chi); \quad \chi = \frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \quad (\text{l-g}) \text{ and}$$

$$P = P^* \exp(-\chi); \quad \chi = \frac{\Delta_{\text{sub}}H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \quad (\text{s-g}),$$

for which we used the assumption that ΔH and ΔV hardly change in the temperature range around the triple point.

With this assumption we can calculate $\Delta_{\text{sub}}H$ using $\Delta_{\text{sub}}H = \Delta_{\text{fus}}H + \Delta_{\text{vap}}H = 10.6 + 30.8 = 41.4 \text{ kJ/mol}$.

$\Delta_{\text{fus}}V$ follows from (benzene C_6H_6 , $M(\text{C}_6\text{H}_6) = 78.11 \text{ g/mol}$)

$$\Delta_{\text{fus}}V = \frac{M}{\rho(l)} - \frac{M}{\rho(s)} = \frac{78.11}{0.879} - \frac{78.11}{0.891} = 1.197 \text{ cm}^3/\text{mol}.$$

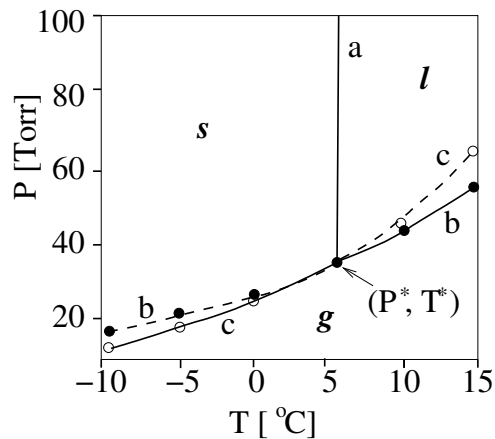
Entering these values we can find the three phase boundary lines (1 Torr = 133.322 Pa)

$$P = P^* + \frac{10.6 \cdot 10^3}{1.197 \cdot 10^{-6}} \ln \frac{T}{T^*} = P^* + 8.855 \cdot 10^9 \text{ [Pa]} \ln \frac{T}{T^*} = P^* + 6.64 \cdot 10^7 \text{ [Torr]} \ln \frac{T}{T^*} \quad (\text{s-l}),$$

$$P = P^* \exp(-\chi); \quad \chi = \frac{30.8 \cdot 10^3}{8.314} \left(\frac{1}{T} - \frac{1}{T^*} \right) = 3705 \text{ [K]} \left(\frac{1}{T} - \frac{1}{T^*} \right) \quad (\text{l-g}) \text{ en}$$

$$P = P^* \exp(-\chi); \quad \chi = \frac{41.4 \cdot 10^3}{8.314} \left(\frac{1}{T} - \frac{1}{T^*} \right) = 4980 \text{ [K]} \left(\frac{1}{T} - \frac{1}{T^*} \right) \quad (\text{s-g}).$$

These lines can be found in the figure below as *a*, *b* en *c*, around the triple point of $P^* = 36 \text{ Torr}$ and $T^* = 5.50 \text{ }^\circ\text{C}$. The boundary line of *c* for $T > T^*$ (dashed line) is metastable, and the same applies to *b* for $T < T^*$.



Exercise 8

- a) The suggested Maxwell relation with a term $\left(\frac{\partial V}{\partial T}\right)_P = V\alpha$ follows from $dG = VdP - SdT$.

G is a state function with independent variables P and T , which means that

$$\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial^2 G}{\partial P \partial T}, \text{ and therefore } \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T.$$

According to this relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -V\alpha$, and therefore $dS|_T = -V\alpha dP|_T$.

The volume is $V = \frac{M}{\rho}n = \frac{200}{2 \cdot 10^3} \cdot 1 = 0.1 \text{ l}$ for 1 mol.

If we assume that α is independent of the pressure we find (note the units)

$$\Delta S = -V\alpha\Delta P = -0.1 \cdot 2 \cdot 10^{-3} (100 - 1) = -0.02 \text{ l} \cdot \text{bar} \cdot \text{K}^{-1} = -0.02 \cdot 10^2 \text{ m}^3 \text{Pa} \cdot \text{K}^{-1} = -2 \text{ J} \cdot \text{K}^{-1}$$

- b) $\Delta U = W + Q = -\int P_{ext.} dV + Q \approx Q$ because the volume change is negligible.
 In that case the difference between a reversible and an irreversible process is also negligible, and since U is a state function we find:
 $\Delta U \approx Q^{rev} = T\Delta S = -300 \cdot 2 = -0.6 \text{ kJ}$.
- c) $dH = dU + PdV + VdP = dQ + VdP$, so
 $\Delta H \approx Q + \int VdP \approx Q + V\Delta P$ because the volume change is negligible, so
 $\Delta H = -600 + 0.1 \cdot 10^{-3}(100 - 1) \cdot 10^5 \text{ J} = 0.4 \text{ kJ}$.
- d) $dA = dU - TdS - SdT = -PdV - SdT$, so
 $\Delta A \approx 0$ because it is an isothermal process and the volume change is negligible.
- e) $dG = dA + PdV + VdP = -SdT + VdP$, so
 $\Delta G \approx V\Delta P$ because it is an isothermal process and the volume change is negligible.
 $\Delta G = 0.1 \cdot 10^{-3}(100 - 1) \cdot 10^5 \text{ J} = 1 \text{ kJ}$.

Exercise 9

- a) Since a second order phase transition has $\Delta V = \Delta S = 0$ we would find $\frac{dP}{dT} = \frac{0}{0}$ for the Clapeyron equation.
- b) The thermal expansion coefficient and the isothermal compressibility are given by

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{and} \quad \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T.$$

A change in the volume $V = V(T, P)$ is given by

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP = \alpha V dT - \kappa_T V dP.$$

This equation applies to both phases (1 and 2). The volume V is a continuous function for a second order phase transition, which implies that along the phase boundary line

$$dV_1 = dV_2, \quad \text{so} \quad \alpha_1 dT - \kappa_{T,1} dP = \alpha_2 dT - \kappa_{T,2} dP \quad \text{and therefore}$$

$$\frac{dP}{dT} = \frac{\alpha_2 - \alpha_1}{\kappa_{T,2} - \kappa_{T,1}}.$$

We derive the second Ehrenfest equation from the molar entropy $S_m = S_m(T, P)$

$$dS_m = \left(\frac{\partial S_m}{\partial T} \right)_P dT + \left(\frac{\partial S_m}{\partial P} \right)_T dP = \frac{C_{P,m}}{T} dT - \alpha V_m dP,$$

where we used the suggested relation (which applies to any equilibrium situation)

$$\left(\frac{\partial S_m}{\partial T} \right)_P = \frac{C_{P,m}}{T},$$

for the first term and the Maxwell relation derived in exercise 9a for the second term.

The expression for dS_m applies to both phases. Furthermore, as S_m is a continuous function for a second order phase transition, we find

$$\frac{C_{P,m,1}}{T} dT - \alpha_1 V_m dP = \frac{C_{P,m,2}}{T} dT - \alpha_2 V_m dP,$$

and therefore

$$\frac{dP}{dT} = \frac{C_{P,m,2} - C_{P,m,1}}{TV_m (\alpha_2 - \alpha_1)}.$$