# Answers Tutorials 2 Thermodynamics 2, 2025/2026

Exercise 5

The corrected phase diagram is shown in the figure below, with the corrections in red. The 5 mistakes are:

1. P and T have been swapped
2. l and g have been swapped
3. 'sublimation point' should be 'triple point'
4. the critical point is where the l, g phase boundary line ends
5. the error in the red circle needs clarification. In the red circle four phase boundary lines come together in a single point. This is not possible according to Gibbs' phase rule, $F = C - P + 2$, as four phases $(s_3, s_4, s_5$ and l would be mutually in equilibrium, so $P = 4$, while $C = 1$ because we are dealing with a pure compound (with a unary phase diagram). This would result in $F = C - P + 2 = 1 - 4 + 2 = -1$, so not allowed; A pure compound cannot have four phases in mutual equilibrium.
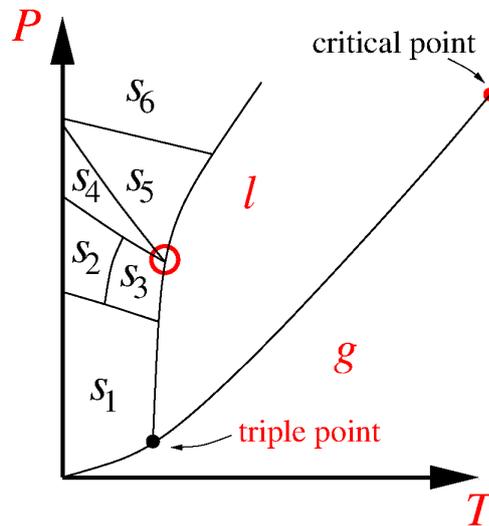
Exercise 6

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:

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

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

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 $T = 303$ K $= 30$ °C.

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):

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

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

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

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 $\Delta_{\text{sub}} H = \Delta_{\text{fus}} H + \Delta_{\text{vap}} H = 10.6 + 30.8 = 41.4$ kJ/mol.

$\Delta_{\text{fus}} V$ follows from (benzene $C_6 H_6$, $M(C_6 H_6) = 78.11$ g/mol)

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

Entering these values and changing all of them to SI (mksA) units, except for the pressures, which we leave in Torr (1 Torr = 133.322 Pa), we can find the three phase boundary lines by plugging in the temperatures in Kelvin. For (T^*, P^*) we can choose the triple point values (278.65 K, 36 Torr).

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

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

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

The three lines can be found in the figure below as a, b en c, around the triple point of $P^* = 36$ Torr (4.800 kPa) and $T^* = 5.50\,°C$ (278.65 K). The boundary line of c for $T > T^*$ (dashed line) is metastable, and the same applies to b for $T < T^*$.
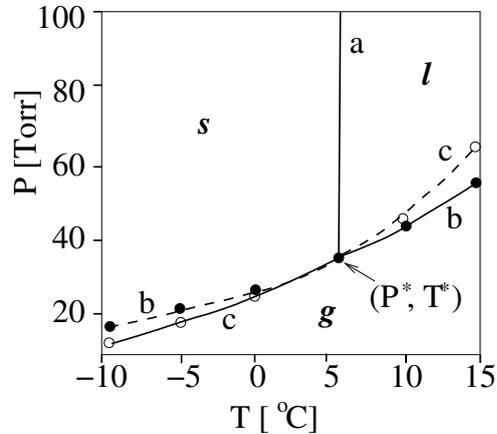
Exercise 8

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

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{fus}}S}{\Delta_{\mathrm{fus}}V} = \frac{\Delta_{\mathrm{fus}}H}{T_{\mathrm{fus}}\Delta_{\mathrm{fus}}V}, \quad \text{so} \quad \mathrm{d}P = \frac{\Delta_{\mathrm{fus}}H}{T_{\mathrm{fus}}\Delta_{\mathrm{fus}}V}\mathrm{d}T \quad \text{and} \quad \int_{P_1}^{P_2}\mathrm{d}P = \int_{T_{\mathrm{fus}}}^{T_{\mathrm{fus},2}} \frac{\Delta_{\mathrm{fus}}H}{T_{\mathrm{fus}}\Delta_{\mathrm{fus}}V}\mathrm{d}T.$$

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 $\mathrm{d}P_{\mathrm{fus}}$ and $\mathrm{d}T_{\mathrm{fus}}$ instead of $\mathrm{d}P$ and $\mathrm{d}T$. 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

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

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

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

This results in a temperature $T_{\mathrm{fus},2} = 234.4$ 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 9

a) The suggested Maxwell relation with a term $\left(\frac{\partial V}{\partial T}\right)_P = V\alpha$ follows from
$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T$.
G is a state function with independent variables P and T, which means that
$\frac{\partial^2 G}{\partial T\partial P} = \frac{\partial^2 G}{\partial P\partial T}$, 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 $\mathrm{d}S|_T = -V\alpha\mathrm{d}P|_T$.
The volume is $V = \frac{M}{\rho}n = \frac{200}{2\cdot 10^3} \cdot 1 = 0.1$ l for 1 mol.
If we assume that α is independent of the pressure we find (note the units)
$\Delta S = -V\alpha\Delta P = -0.1 \cdot 2 \cdot 10^{-3}(100-1) = -0.02\ \mathrm{l\cdot bar\cdot K^{-1}} = -0.02 \cdot 10^2\ \mathrm{m^3 Pa\cdot K^{-1}} = -2\ \mathrm{J\cdot K^{-1}}$

b) $\Delta U = W + Q = -\int P_{ext.}\mathrm{d}V + Q \approx Q$ 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:
$\Delta U = Q^{rev} = T\Delta S = -300 \cdot 2 = -0.6$ kJ.

c) $\mathrm{d}H = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P = \mathrm{d}Q + V\mathrm{d}P$, so
$\Delta H = Q + \int V\mathrm{d}P \approx Q + V\Delta P$ because the volume change is negligible, so
$\Delta H = -600 + 0.1 \cdot 10^{-3}(100-1) \cdot 10^5 \mathrm{J} = 0.4$ kJ.

d) $\mathrm{d}A = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T = -P\mathrm{d}V - S\mathrm{d}T$, so
$\Delta A \approx 0$ because it is an isothermal process and the volume change is negligible.

e) $\mathrm{d}G = \mathrm{d}A + P\mathrm{d}V + V\mathrm{d}P = -S\mathrm{d}T + V\mathrm{d}P$, so
$\Delta G \approx V\Delta P$ because it is an isothermal process and the volume change is negligible.
$\Delta G = 0.1 \cdot 10^{-3}(100-1) \cdot 10^5 \mathrm{J} = 1$ kJ.