# Answers Tutorials 2 Thermodynamics 2, 2024/2025

## 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.
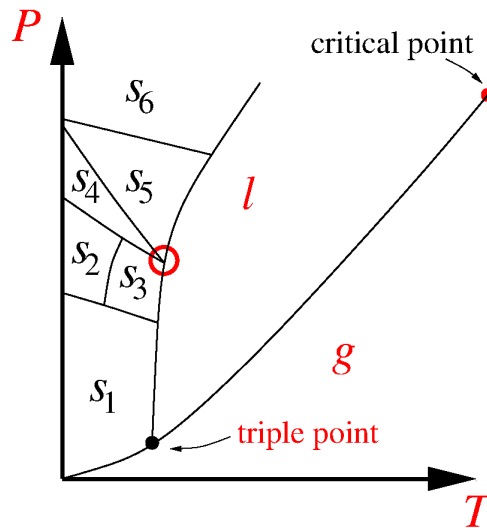


## Exercise 6

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):

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

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

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

for which we used the assumption that $\Delta H$ and $\Delta V$ 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 $C_6H_6$, $M(C_6H_6) = 78.11$ 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).

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

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

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

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 $T < T^*$.
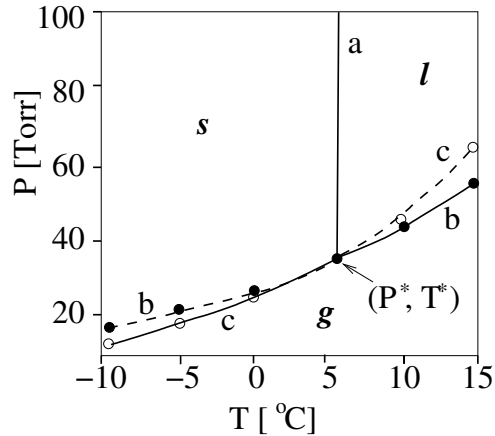
# Exercise 8

The change in freezing point as a result of the higher pressure in the mercury column can be calculated with the Clapeyron equation (use $\Delta_{\text{fus}}G = \Delta_{\text{fus}}H - T_{\text{fus}}\Delta_{\text{fus}}S = 0$ 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 $dP_{\text{fus}}$ and $dT_{\text{fus}}$ instead of $dP$ and $dT$. We assume that for the small temperature change all quantities in the integral (except for $T_{\text{fus}}$ 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 $\Delta P = (P_2 - P_1) = \rho(\text{l})g\Delta h$, with $\Delta h$ 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

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

This results in a temperature $T_{\text{fus},2} = 234.4$ 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
$dG = VdP - SdT$.
$G$ is a state function with independent variables $P$ and $T$, which means that
$\frac{\partial^2 G}{\partial T\partial P} = \frac{\partial^2 G}{\partial P\partial T}$, 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 $V = \frac{M}{\rho}n = \frac{200}{2\cdot 10^3}\cdot 1 = 0.1$ l for 1 mol.
If we assume that $\alpha$ is independent of the pressure we find (note the units)
$\Delta S = -V\alpha\Delta P = -0.1\cdot 2\cdot 10^{-3}(100-1) = -0.02$ l·bar·K$^{-1}$ = $-0.02\cdot 10^2$ m$^3$Pa·K$^{-1}$ = $-2$ J·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:
$\Delta U = Q^{rev} = T\Delta S = -300\cdot 2 = -0.6$ kJ.

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