

Thermodynamics tutorhour 5

December 6th 2023

Questions about the lecture or course matter?
Phase and chemical equilibrium

Phase transitions and the phase diagram

For example:

at boiling point (T_{boil}) the **liquid phase** and **gas phase** are in equilibrium : $\mu_l = \mu_g$

and: $d\mu_l = d\mu_g$

Gibbs-Duhem: $d\mu = -S_m dT + V_m dp$

$$d\mu_l = d\mu_g$$

$$-S_{m(l)} dT + V_{m(l)} dp =$$

$$(S_{m(g)} - S_{m(l)}) dT$$

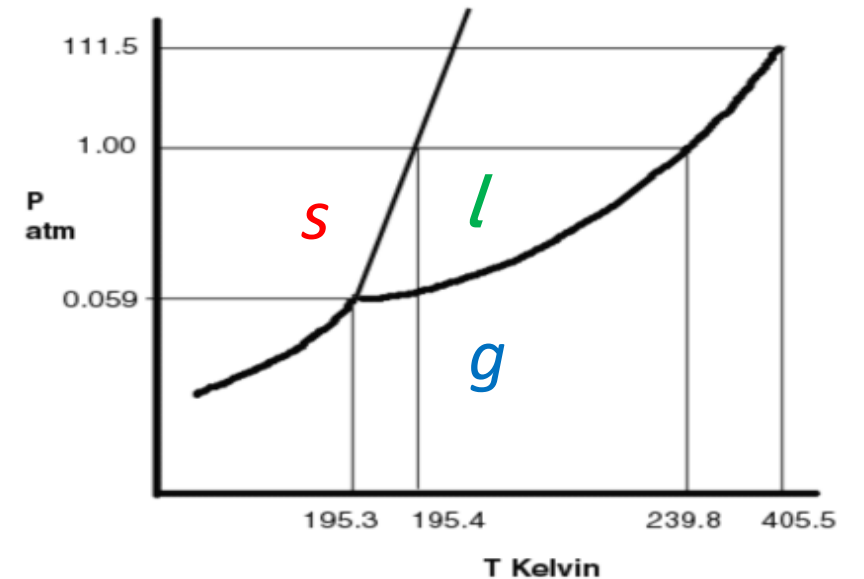
$$\Delta_{trs} S$$

$$\Delta_{trs} S = \frac{\Delta_{trs} H}{T}$$

$$\Delta_{trs} V$$

$$\frac{dp}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V} = \frac{\Delta_{trs} H}{\Delta_{trs} V \cdot T}$$

This expression for the slope in a phase diagram holds for **all** phase transitions!



For all phase transitions holds: $\frac{dp}{dT} = \frac{\Delta_{trs}H}{\Delta_{trs}V \cdot T}$

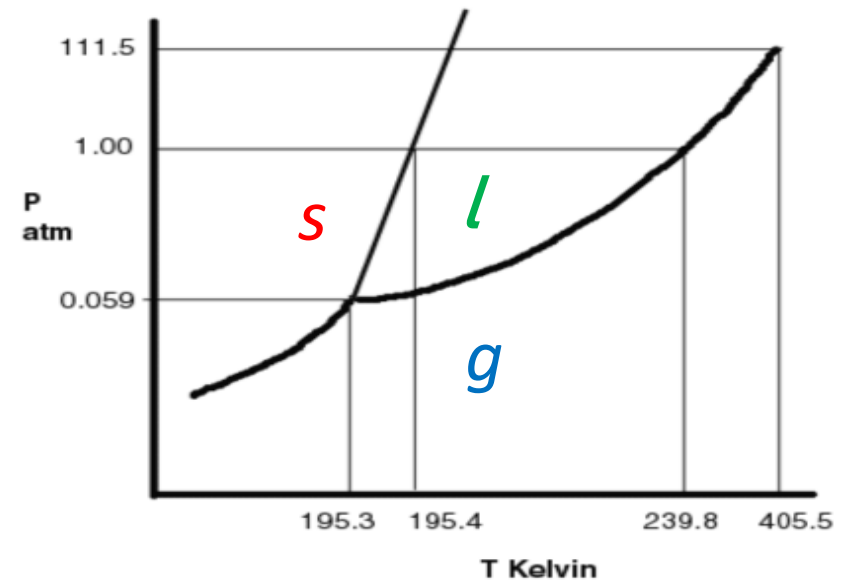
Question 1: From this relation, derive an expression for Δp ($= p_2 - p_1$) in terms of T_1 and T_2 for the **solid/liquid** phase boundary.

$$dp = \frac{\Delta_{trs}H}{\Delta_{trs}V} \cdot \frac{1}{T} dT$$

$$\int dp = \int \frac{\Delta_{trs}H}{\Delta_{trs}V} \cdot \frac{1}{T} dT$$

$$\int dp = \frac{\Delta_{trs}H}{\Delta_{trs}V} \int \frac{1}{T} dT$$

$$\Delta p = \frac{\Delta_{trs}H}{\Delta_{trs}V} \ln \frac{T_2}{T_1}$$



For all phase transitions holds: $\frac{dp}{dT} = \frac{\Delta_{trs}H}{\Delta_{trs}V \cdot T}$

If we go from **solid/liquid** to **gas** we may assume: $V_{\text{gas}} \gg V_{\text{liquid}} \approx V_{\text{solid}}$
 $\Delta_{\text{trs}}V \approx V_{\text{m}} = RT / p$

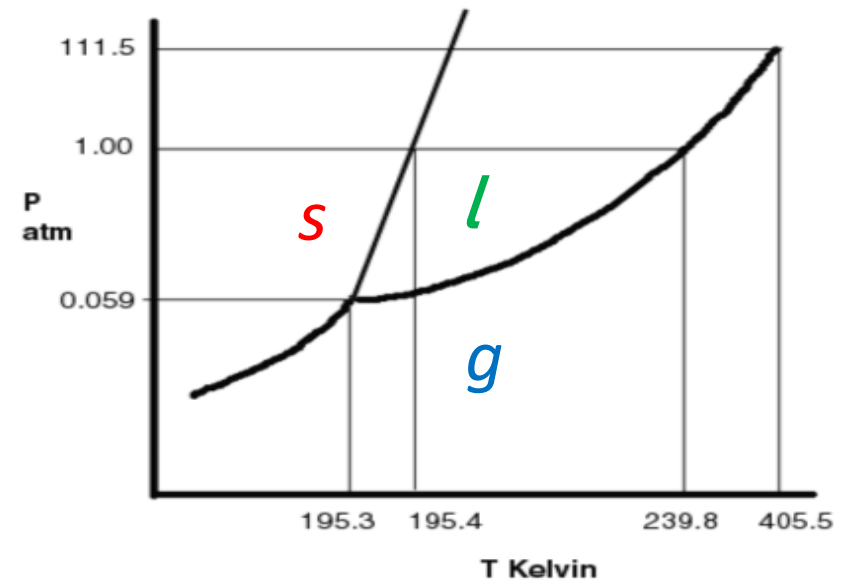
The expression for the slope changes to:

$$\frac{dp}{dT} = \frac{\Delta_{\text{trs}}H \cdot p}{T \cdot RT}$$

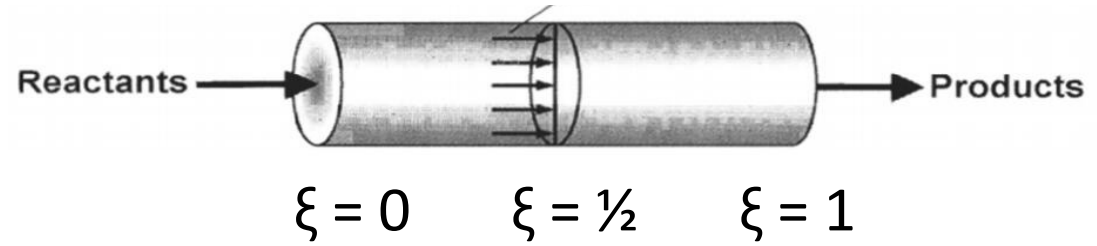
Question 2: From this, derive an expression for $\ln \frac{p_2}{p_1}$ in terms of T_1 and T_2 for the **solid/gas** and **liquid/gas** phase boundaries.

$$\frac{1}{p} dp = \frac{\Delta_{\text{trs}}H}{R} \cdot \frac{1}{T^2} dT$$

$$\int \frac{1}{p} dp = \int \frac{\Delta_{\text{trs}}H}{R} \cdot \frac{1}{T^2} dT \quad \text{so} \quad \ln \frac{p_2}{p_1} = -\frac{\Delta_{\text{trs}}H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$



ξ is the extent of the reaction



Molar fraction: $x_i = \frac{\text{number of moles of component } i}{\text{total number of moles}}$

Partial pressure: $p_i = \frac{\text{pressure of component } i}{\text{total pressure}}$

For a perfect gas holds: $p_i = x_i \cdot p_{tot}$

$$\Delta_r G = \Delta_r G^\theta + RT \ln \prod_i \left(\frac{p_i}{p^\theta} \right)^{\nu_i} = \Delta_r G^\theta + RT \ln Q$$

Given the following reaction: $4 \text{NH}_3(\text{g}) + 3 \text{O}_2(\text{g}) \rightleftharpoons 2 \text{N}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$

Question 3: Give the expression for Q using what you learned in high school.

$$Q = \frac{[\text{N}_2]^2 \cdot [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 \cdot [\text{O}_2]^3}$$

Question 4: Rewrite this expression using partial pressures.

$$Q = \frac{\left(\frac{p_{\text{N}_2}}{p^\theta} \right)^2 \cdot \left(\frac{p_{\text{H}_2\text{O}}}{p^\theta} \right)^6}{\left(\frac{p_{\text{NH}_3}}{p^\theta} \right)^4 \cdot \left(\frac{p_{\text{O}_2}}{p^\theta} \right)^3}$$

Given the following reaction: $4 \text{NH}_3(\text{g}) + 3 \text{O}_2(\text{g}) \rightleftharpoons 2 \text{N}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$

$$\Delta_r G = \Delta_r G^\theta + RT \ln Q \quad \text{with} \quad Q = \frac{\left(\frac{p_{\text{N}_2}}{p^\theta}\right)^2 \cdot \left(\frac{p_{\text{H}_2\text{O}}}{p^\theta}\right)^6}{\left(\frac{p_{\text{NH}_3}}{p^\theta}\right)^4 \cdot \left(\frac{p_{\text{O}_2}}{p^\theta}\right)^3}$$

At **equilibrium** holds: $\Delta_r G = 0$ and $Q = K_p$

Leading to: $\Delta_r G^\theta = -RT \ln K_p$

Need to know for an **ideal mixture**:

$$\Delta_{mix} G = nRT(x_1 \ln x_1 + x_2 \ln x_2) < 0$$

$$\Delta_{mix} S = -nR(x_1 \ln x_1 + x_2 \ln x_2) > 0$$

Question 5: Show mathematically that for all possible values of x_1 and x_2 holds:

$$\Delta_{mix} G < 0 \text{ and } \Delta_{mix} S > 0.$$

- x_1 and x_2 are the mole fractions and can only have values between 0 and 1
- $x = 0$ and $x = 1$ are not allowed, because in that case there would be no mixing
- so the term $x \ln x$ is negative for all possible values of x_1 and x_2
- leading to $\Delta_{mix} G < 0$ and $\Delta_{mix} S > 0$ QED