Physical Chemistry I. practice

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IV.: Phase transitions of ideal one-component systems

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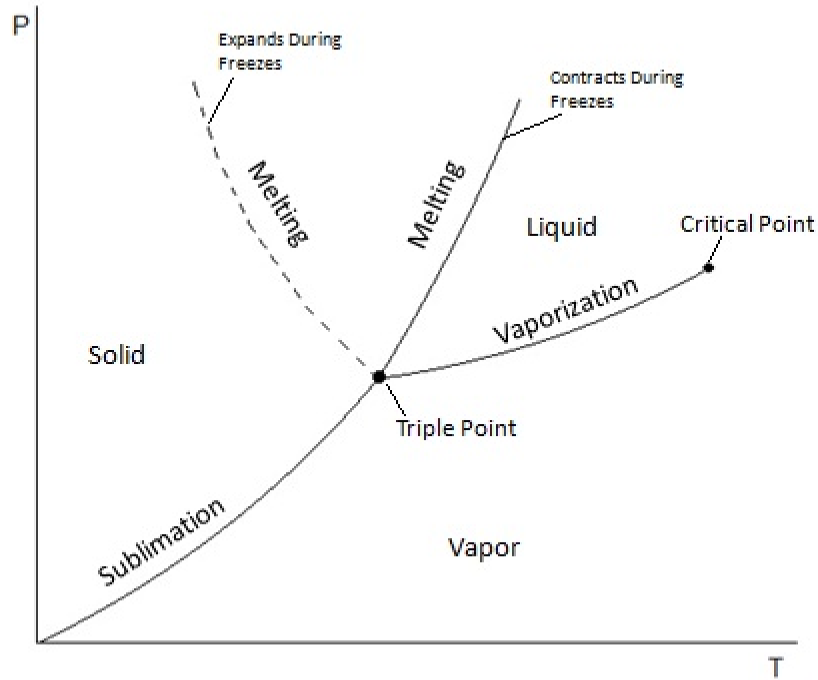
http://oktatas.ch.bme.hu/oktatas/konyvek/fizkem
/PysChemBSC1/Requirements.pdf
http://oktatas.ch.bme.hu/oktatas/konyvek/fizkem
/PysChemBSC1/Important_dates.pdf

p-T diagram



Clapeyron:
$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H}{T\Delta V}$$

Clausius-Clapeyron:
$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\lambda p}{T^2 R}$$
$$\rightarrow ln\frac{p_2}{p_1} = -\frac{\lambda}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$T, \Delta H, \Delta V$: Temperature, enthalpy change and volume change during phase transition

λ: Latent heat, T-independent ΔH

$\Delta H, \lambda$, and ΔV can be either molar $(\frac{J}{mol}, \frac{m^3}{mol})$ or specific $(\frac{J}{kg}, \frac{m^3}{kg})$ changes

Clapeyron vs. Clausius-Clapeyron

Calculate the heat of vaporization of benzene at $p = 101,3\mathrm{k}Pa$.

$T_v(101,3\ \mathrm{k}Pa) = 80,1°C$

$\frac{\mathrm{d}T_v}{\mathrm{d}p} = 0,32\frac{K}{\mathrm{k}Pa}$ (around 1 bar)

$\rho_{vap.} = 2,741\ \frac{\mathrm{kg}}{\mathrm{m}^3}$

$\rho_{liq.} = 814,4\ \frac{\mathrm{kg}}{\mathrm{m}^3}$

$$\frac{\mathrm{d}p}{\mathrm{d}T_v} = \frac{1}{\frac{\mathrm{d}T_v}{\mathrm{d}p}} = 3,125\ \frac{\mathrm{k}Pa}{K}$$

Clapeyron: $\underline{\Delta H} = \frac{\mathrm{d}p}{\mathrm{d}T_v} \cdot T_v(101,3\ \mathrm{k}Pa) \cdot \left(\frac{1}{\rho_{vap.}} - \frac{1}{\rho_{liq.}}\right)$

$$3,125\ \frac{\mathrm{k}Pa}{K} \cdot 353,25\ K \cdot \left(\frac{1}{2{,}741\ \frac{\mathrm{kg}}{\mathrm{m}^3}} - \frac{1}{814{,}4\ \frac{\mathrm{kg}}{\mathrm{m}^3}}\right) = \underline{401\ \frac{\mathrm{k}J}{\mathrm{k}g}}$$

Clausius-Clapeyron: $\underline{\lambda} = \frac{\mathrm{d}p}{\mathrm{d}T_v} \cdot [T_v(101,3\ \mathrm{k}Pa)]^2 \cdot R \cdot \frac{1}{p}$

$$3,125\ \frac{\mathrm{k}Pa}{K} \cdot (353,25\ K)^2 \cdot 8,314\frac{J}{mol\ K} \cdot \frac{1}{101{,}3\ \mathrm{k}Pa} = 32\ \frac{\mathrm{k}J}{mol}$$

= (since 1 kg Benzene = 12,82 mol) $\underline{410\ \frac{\mathrm{k}J}{\mathrm{k}g}}$

Clausius-Clapeyron

n-octane has

$p_1 =$26660 Pa eq. vapor pressure at $T_1 =$83,52 °C

$p_2 =$39990 Pa eq. vapor pressure at $T_2 =$95,16 °C

What is the p_3 eq. vapor pressure at $T_3 =$90 °C?

Use the Clausius-Clapeyron approximation!

Clausius-Clapeyron

First we need λ: use Clausius-Clapeyron

$$\lambda = \frac{-ln\frac{p_2}{p_1} \cdot R}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{-ln\frac{39{,}9\ \mathrm{k}Pa}{26{,}6\ \mathrm{k}Pa} \cdot R}{\frac{1}{368{,}31\ K} - \frac{1}{356{,}67\ K}} = 38044 \frac{J}{mol}$$

Now we can calculate p_3 with Clausius-Clapeyron:

$$\underline{p_3} = p_1 \cdot e^{-\frac{\lambda}{R} \cdot \left(\frac{1}{T_3} - \frac{1}{T_1}\right)} = 26,6\,\mathrm{k}Pa \cdot e^{-\frac{38044\ J/mol}{R} \cdot \left(\frac{1}{363{,}15\ K} - \frac{1}{356{,}67\ K}\right)}$$

$$= \underline{33,52\ \mathrm{k}Pa}$$

Clapeyron

The melting point of acetic acid as a function of the pressure is given as (p in Pa):

$$T_m(p) = 16,66°C + 0,231 \cdot 10^{-6}\frac{°C}{Pa} \cdot p - 2,25 \cdot 10^{-16}\frac{°C}{Pa^2} \cdot p^2$$

a) What is ΔH_f at standard pressure ($10^5\ Pa$) if $\Delta V_f = 0,156\ \frac{\mathrm{d}m^3}{\mathrm{kg}}$?

We need $\frac{\mathrm{d}p}{\mathrm{d}T_m}$ and T_m for Clapeyron

$$\frac{\mathrm{d}p}{\mathrm{d}T_m} = \frac{1}{\frac{\mathrm{d}T_m}{\mathrm{d}p}} = \frac{1}{2{,}31 \cdot 10^{-7}\frac{°C}{Pa} + 4{,}5 \cdot 10^{-16}\frac{°C}{Pa^2} \cdot p} = 4,328 \cdot 10^6 \frac{Pa}{°C} = 4,328 \cdot 10^6 \frac{Pa}{K}$$

$$T_m(10^5\ Pa) = 16,683°C$$

$$\underline{\Delta H_f} = \frac{\mathrm{d}p}{\mathrm{d}T_m} \cdot T_m \cdot \Delta V_f = 4,328 \cdot 10^6 \frac{Pa}{K} \cdot 289,833\ K \cdot 1,56 \cdot 10^{-4}\frac{m^3}{\mathrm{kg}}$$

$$= \underline{196\ \frac{\mathrm{k}J}{\mathrm{kg}}}$$

Clapeyron

The melting point of acetic acid as a function of the pressure is given as (p in Pa):

$$T_m(p) = 16,66°C + 0,231 \cdot 10^{-6} \frac{°C}{Pa} \cdot p - 2,25 \cdot 10^{-16} \frac{°C}{Pa^2} \cdot p^2$$

a) What is ΔH_f at 100 MPa pressure if $\Delta V_f = 0,115 \ \frac{\mathrm{d}m^3}{\mathrm{k}g}$?

Clapeyron

We need $\frac{\mathrm{d}p}{\mathrm{d}T_m}$ and T_m for Clapeyron

$$p = 10^8 Pa$$

$$\underline{T_m(10^8 Pa)} = 16,66°C + 0,231 \cdot 10^{-6} \frac{°C}{Pa} \cdot 10^8 Pa$$

$$-2,25 \cdot 10^{-16} \frac{°C}{Pa^2} \cdot 10^{16} Pa^2 = \underline{37,51°C}$$

$$\frac{\mathrm{d}p}{\mathrm{d}T_m} = \frac{1}{\frac{\mathrm{d}T_m}{\mathrm{d}p}} = \frac{1}{2{,}31 \cdot 10^{-7} \frac{°C}{Pa} + 4{,}5 \cdot 10^{-16} \frac{°C}{Pa^2} \cdot p} = 5,376 \cdot 10^6 \frac{Pa}{K}$$

$$\underline{\Delta H_f} = \frac{\mathrm{d}p}{\mathrm{d}T_m} \cdot T_m \cdot \Delta V_f = 5,376 \cdot 10^6 \frac{Pa}{K} \cdot 310,66\ K \cdot 1,15 \cdot 10^{-4} \frac{m^3}{\mathrm{k}g}$$

$$= \underline{192\ \frac{\mathrm{k}J}{\mathrm{k}g}}$$

Application

From the 10 °C street we go into a room with 20 °C temperature and 60% relative humidity. Will our glasses get steamed?

Eq. vapor pressure of water at 20 °C is 2,3 kPa

$\lambda_v = 40,7\ \mathrm{k}J/mol$, steam is ideal gas

Question: is the partial pressure of water in the room higher than the eq. vapor pressure for 10 °C? If yes, the vapor will conensate on the glasses

$$\underline{p_1} = \frac{p_2}{e^{-\frac{\lambda_v}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}} = \frac{2{,}3\ \mathrm{k}Pa}{e^{-\frac{40700\ \ J/mol}{R}\left(\frac{1}{293{,}15\ \ K}-\frac{1}{283{,}15\ \ K}\right)}}$$

$$= \underline{1,275\ \mathrm{k}Pa} < 0,6 \cdot 2,3\ \mathrm{k}Pa = \underline{1,38\ \mathrm{k}Pa}$$