# Physical Chemistry I. practice

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IV.: Phase transitions of ideal one-component systems

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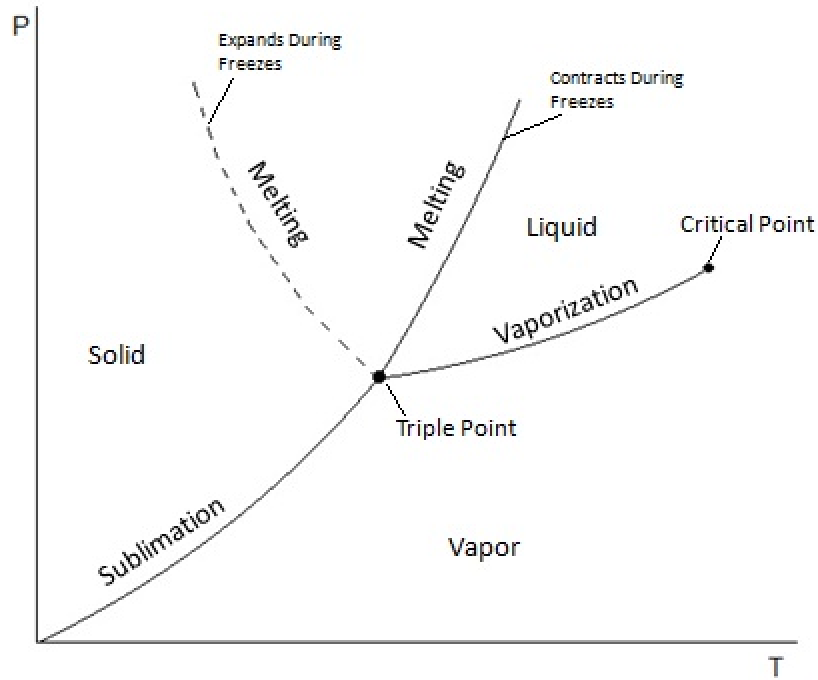
# p-T diagram




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

$\lambda$: Latent heat, T-independent $\Delta H$

$\Delta H, \lambda$, and $\Delta V$ 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 $bar$)

$\rho_{vap.} = 2.741\ \frac{\mathrm{kg}}{\mathrm{m}^3}$

$\rho_{liq.} = 814.4\ \frac{\mathrm{kg}}{\mathrm{m}^3}$

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$$\frac{\mathrm{d}p}{\mathrm{d}T_v} = \frac{1}{\frac{\mathrm{d}T_v}{\mathrm{d}p}} = 3.125\ \frac{\mathrm{k}Pa}{K}$$

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 k$g$ 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 $\lambda$: 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 $\Delta H_f$ at standard pressure ($10^5$ $Pa$) if $\Delta V_f = 0.156 \frac{\mathrm{d}m^3}{\mathrm{kg}}$?

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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 $\Delta H_f$ at 100 M$Pa$ 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 k$Pa$

$\lambda_v = 40.7\ \mathrm{k}J/mol$, steam is ideal gas

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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

$$\underline{p_1} = \frac{p_2}{e^{-\frac{\lambda_v}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}} = \frac{2.3\ \mathrm{k}Pa}{e^{-\frac{40700\ \ J/mol}{R}\left(\frac{1}{293.15\ \ K}-\frac{1}{283.15\ \ K}\right)}}$$

$$= \underline{1.275\ \mathrm{k}Pa} < 0.6 \cdot 2.3\ \mathrm{k}Pa = \underline{1.38\ \mathrm{k}Pa}$$