

## WEEK 3

### The Clapeyron Equation

At equilibrium the chemical potential between two phases A and B are equal.

$$\begin{aligned}\mu^A &= \mu^B \\ \Rightarrow d\mu^A &= d\mu^B\end{aligned}$$

Using this and the definition of Chemical Potential ( $\mu = -S_m dt + V_m dT$ ) we can derive the Clapeyron Equation

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m},$$

which since  $\Delta G = \Delta H - T\Delta S = 0$  at equilibrium can also be expressed as

$$\frac{dp}{dT} = \frac{\Delta H_m}{T\Delta V_m}.$$

### Using the Clapeyron to justify the general shape of a $p$ - $V$ phase diagram

#### **Estimate the slope of the solid/liquid co-existence line.**

Difficult to measure  $\Delta_{\text{fus}}S_m$ , but  $\Delta_{\text{fus}}H_m$  is known for almost everything. For our estimation purposes, take the average  $\Delta_{\text{fus}}H_m$  or several common compounds, average them and then use the equilibrium condition to convert them into  $\Delta_{\text{fus}}S_m$

This gives an average  $\Delta_{\text{fus}}S_m$  of  $22 \text{ J K}^{-1} \text{ mol}^{-1}$ .

Typically the change in volume on melting is tiny. Again, average over several common compounds is  $\Delta_{\text{fus}}V_m = 2 \times 10^{-6} \text{ m}^3$ .

Thus gives an average slope of  $dp/dT = 5.5 \times 10^6 \text{ Pa K}^{-1} = 55 \text{ bar K}^{-1}$ .. (*i.e.*, very steep).

#### **Estimate the slope of the liquid/gas co-existence line.**

Similarly, it is difficult to measure  $\Delta_{\text{vap}}S_m$ , but  $\Delta_{\text{vap}}H_m$  is known for almost everything. Averaging  $\Delta_{\text{vap}}H_m$  and converting into  $\Delta_{\text{fus}}S_m$  as above gives  $\Delta_{\text{vap}}S_m$  of  $95 \text{ J K}^{-1} \text{ mol}^{-1}$ .

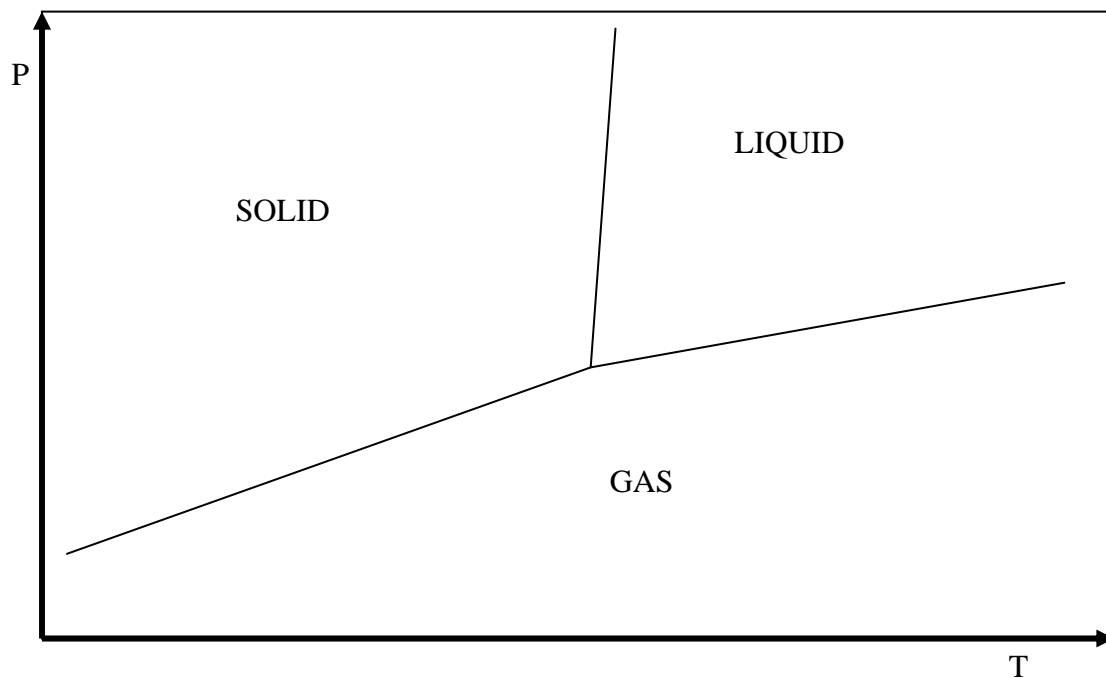
Molar volume of a gas near room temperature is about  $20 \text{ L} = 2 \times 10^{-2} \text{ m}^3$ . The molar volume of a typical liquid is *ca.*  $20 \text{ mL}$ . Thus to a good approximation  $\Delta_{\text{vap}}V_m = 20 \text{ L}$ .

Thus gives an average slope of  $dp/dT = 5000 \text{ Pa K}^{-1} = 5 \times 10^{-2} \text{ bar K}^{-1}$ . (*i.e.*, rather shallow).

#### **Estimate the slope of the solid/gas co-existence line.**

Entropy is a state function. Therefore, the path from solid to gas is irrelevant, which means that  $\Delta_{\text{sub}}S_m = \Delta_{\text{fus}}S_m + \Delta_{\text{vap}}S_m$ . This is approximately 1.2 times greater than  $\Delta_{\text{vap}}S_m$ . Since, to a very good approximation,  $\Delta_{\text{vap}}V_m = \Delta_{\text{sub}}V_m$ , the slope of  $dp/dT$  for the solid/gas line will be approximately 1.2 times greater than the liquid/gas line.

**Qualitative  $p$ - $T$  phase diagram based on the above.**



With the Clapeyron we can map the phase diagram for any compound.

### **Increasing the melting and boiling points by increasing the pressure**

If we invert the slope for the solid/liquid line we get  $dT/dp = 0.02 \text{ K bar}^{-1}$ . This implies that to increase the melting point of a solid by 1 K we must increase the pressure by about 50 bar.

Similarly, if we invert the slope of the liquid/gas line  $dT/dp = 20 \text{ K bar}^{-1}$ , which implies if we double the pressure from 1 to 2 bar, we increase the boiling point by 20 K. Given that at normal temperatures the rate of a chemical reaction doubles for every 10 K increase in temperature, this explains how pressure cookers dramatically decrease cooking times without there being dangerously high pressures.

## Using the Clapeyron to Calculate Vapour Pressures as a Function of Temperature

**Solid/Liquid line:**

$$\int_{p_i}^{p_f} dp = \int_{T_i}^{T_f} \frac{\Delta_{fus} S_m}{\Delta_{fus} V_m} dt = \frac{\Delta_{fus} H_m}{\Delta_{fus} V_m} \int_{T_i}^{T_f} \frac{1}{T} dt$$

Thus,

$$p_f - p_i = \frac{\Delta_{fus} H_m}{\Delta_{fus} V_m} \ln \frac{T_f}{T_i} = \frac{\Delta_{fus} H_m}{\Delta_{fus} V_m} \ln \frac{T_i + \Delta T}{T_i} \approx \frac{\Delta_{fus} H_m}{\Delta_{fus} V_m} \frac{\Delta T}{T_i}$$

(assuming that over the relatively small temperature range of interest the  $\Delta H$  and  $\Delta V$  are approximately constant and that  $\ln(1 + x) = x$  for small  $x$ ).

**Liquid/Gas line:**

Now, if we also assume (reasonably) that the gas is ideal and that  $\Delta V = V^{gas}$ , the Clapeyron becomes:

$$\frac{dp}{dT} = \frac{\Delta_{vap} S_m}{\Delta_{vap} V_m} \approx \frac{\Delta_{vap} H_m}{TV^{gas}} = \frac{P \Delta_{vap} H_m}{RT^2}$$

Thus,

$$\frac{dP}{P} = \frac{\Delta_{vap} H_m}{R} \frac{dT}{T^2} \Rightarrow \int_{p_i}^{p_f} \frac{1}{P} dp = \frac{\Delta_{vap} H_m}{R} \int_{T_i}^{T_f} \frac{1}{T^2} dT$$

Therefore,

$$\ln \frac{p_f}{p_i} = -\frac{\Delta_{vap} H_m}{R} \left( \frac{1}{T_f} - \frac{1}{T_i} \right)$$

From this equation the enthalpy of vaporisation can be determined by measuring the vapour pressure as a function of temperature.

**Discussion Problem:**

Benzene normally boils at 353.24 K.

The vapour pressure of liquid benzene at 20.0 °C is  $1.00 \times 10^4$  Pa.

The vapour pressure of solid benzene at -44.3 °C is 88.0 Pa.

Benzene's enthalpy of fusion is  $9.95 \text{ kJ mol}^{-1}$ .

Calculate:

$\Delta_{vap} H_m$ ,  $\Delta_{vap} S_m$ , and the triple point temperature and pressure.