

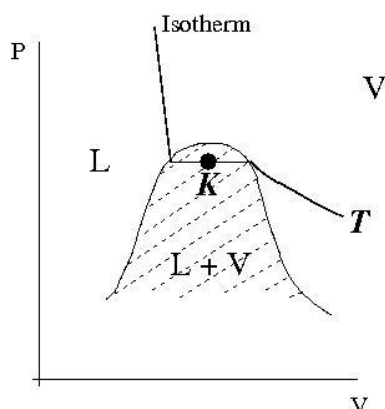
**Tutorial 9: Phase transitions****1. Phases and Clausius-Clapeyron**

- (a) Sketch the P-T projection of the PVT surface for a simple substance and identify its main features.
- (b) By using the fact that the specific Gibbs functions of coexisting phases are the same, derive the Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{l}{T(\nu_2 - \nu_1)}$$

where  $\nu_1$  and  $\nu_2$  are the specific volumes of the two phases and  $l$  is the specific latent heat of the transition.

- (c) In a pressure cooker, food is cooked more quickly by raising the pressure so that water boils at a higher temperature. Estimate the pressure at which water boils at  $130^\circ\text{C}$ . The density of water and steam at  $100^\circ\text{C}$  are  $959\text{ kg m}^{-3}$  and  $0.600\text{ kg m}^{-3}$  respectively, and the latent heat of vaporisation is  $2257\text{ kJ kg}^{-1}$ . Take 1 atmosphere to be  $10^5\text{ N m}^{-2}$ .

**2. Phase mixtures**

The figure shows an isotherm on the  $P-V$  projection. At the point X the substance is a mixture of liquid and vapour. The total mass of substance is the sum of the liquid and vapour masses  $m = m_l + m_v$ . At coexistence  $v_l$  and  $v_v$  are the specific volumes of the liquid and vapour (per kg).

Write down an expression for the total volume at X.

Let the specific volume of the mixture at X be  $v$ . Show that :

$$m_l(v - v_l) = m_v(v_v - v)$$

Explain why this result, which gives the ratio  $m_v/m_l$ , is known as the 'lever rule'.

How does the Gibbs free energy change with volume in the coexistence region?

What is the compressibility of the substance at X.

**3. Solid-solid phase transitions**

Tin can exist in two forms ("allotropes"): Grey tin is the stable form at low temperatures and white tin the stable at high temperatures and pressures. There is a first-order transition between the two phases at  $291\text{ K}$  and  $1\text{ atm}$ . Given the latent heat for the transition ( $18.5 \times 10^3\text{ J kg}^{-1}$ ); and the densities  $5.75 \times 10^3\text{ kg m}^{-3}$  (grey) and  $7.30 \times 10^3\text{ kg m}^{-3}$  (white); estimate the change in this transition temperature if the pressure is increased to  $100\text{ atm}$ ?

*Hint: The grey tin to white tin transition is a phase transition, so use the Clausius Clapeyron equation. Try assuming the phase boundary is a straight line, putting  $dP/dT = \Delta P/\Delta T$  even though  $\Delta P = 99\text{ atm}$ . Note also that the density change going from the low-temperature-stable grey tin to the high-temperature-stable white tin is an increase, like in ice-to-water – so anticipate  $dP/dT$  to be negative.*

**4. Triple Point**

The sublimation and the vaporization curves of a particular material are given by:

$$\ln P = 0.04 - 6/T \quad \text{sublimation}$$

$$\ln P = 0.03 - 4/T \quad \text{vaporization}$$

where  $P$  is in atmospheres.

- (a) Find the temperature and pressure of the triple point.  
 (b) By assuming that the volume in the gas phase is much larger than for the solid or liquid, show that the latent heats are  $4R$  and  $6R$  per mole.  
 (c) By considering entropy around a cycle around the triple point in the  $PT$  phase diagram, show that

$$\frac{l_{SV}}{T_{TP}} - \frac{l_{SL}}{T_{TP}} - \frac{l_{LV}}{T_{TP}} = 0$$

and hence calculate the latent heat of fusion.

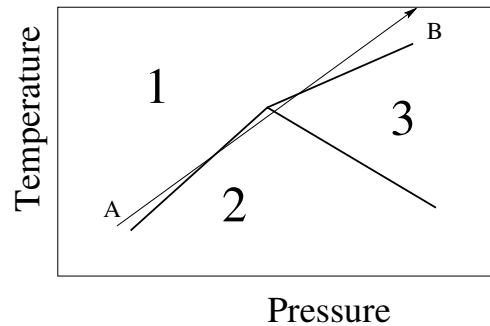
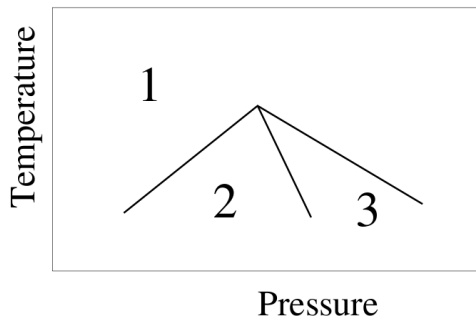
*Hint: Consider a loop round the triple point in the  $PT$  phase diagram. As  $S$  is a state function,*

$$\frac{l_{SV}}{T_{TP}} - \frac{l_{SL}}{T_{TP}} - \frac{l_{LV}}{T_{TP}} = 0$$

### 5. Impossible Phase diagram

Consider the phase diagram shown below on the left, in which three proposed phases are separated by first order phase transitions. A diamond anvil cell experiment applies an isothermal pressure increase which traverses the three phases.

- (a) List the phases 1-3 in order of density. Comment on the compressibilities.  
 (b) By considering isothermal pressure increase just below the triple point, show that this phase diagram is impossible.  
 (c) The diagram on the right represents a shock compression process, along the line AB, which has constant slope  $m$ . Define the quantity (call it  $Z$ ) which conserved along this line. Is this quantity a state variable?  
 (d) By generalising parts (a) and (b) to consider  $Z$  and its conjugate variable, show that no sector of the phase diagram can have an angle greater than 180 degrees at the triple point. You do not need evaluate the conjugate variable.



### 6. Pressure effect on melting ice

Water has the unusual property that the solid phase (ice) can be melted by applying sufficiently large pressure. Use the Clausius-Clapeyron equation to determine the additional pressure above atmospheric  $\Delta P$  required to melt ice at temperature  $-\Delta T$  below freezing (at  $0^\circ C$ ). This value is in effect the slope of the phase boundary in the  $P$ - $T$  representation. Comment on the sign of the value. Take  $l$  the latent heat of fusion to be  $333.7 kJ kg^{-1}$ , and the densities of water and ice at  $0^\circ C$  to be  $\rho_w = 1000 kg m^{-3}$  and  $\rho_i = 916 kg m^{-3}$ .

Assuming the slope of the phase boundary is constant away from the atmospheric melting point of water (which turns out to be a valid assumption), use your calculated value in the following situations.

- (a) Melting glaciers. The bottom surface of a  $2000m$  thick glacier is at a temperature of  $-1.5^\circ C$ . Will the water here be liquid or ice? Use the density of ice given above.  
 (b) Very cold water. The lowest temperature at which liquid water is stable is  $-22^\circ C$ . What pressure must be applied to keep the water from freezing? Write the answer in Pa and atm.  
 (c) Ice skates. Do ice skates apply sufficient pressure on the surface of ice to melt it? You will have to make some assumptions regarding the area of skate in contact with the ice, the temperature and the weight of the skater