

Lecture Contents

4. Physical Transformations of Pure Substances

Phase diagrams

4.1 The stabilities of phases

4.2 Phase boundaries

4.3 Three typical phase diagrams

Phase stability and phase transitions

4.4 The thermodynamic criterion of equilibrium

4.5 The dependence of stability on the conditions

4.6 The location of phase boundaries

4.7 The Ehrenfest classification of phase transitions



Phase diagrams

4.1 The stabilities of phases

Phase of a substance : a form of matter that is uniform in Chemical composition and physical state

Phase transition : the spontaneous conversion of one phase into another phase

Transition temperature (T_{trs}) : the temperature at which two phases are at equilibrium and G is minimized at a given p

Metastable phase : thermodynamically unstable phase that persist because the transition to stable phase is kinetically hindered.
ex) diamond (a metastable phase of C)

4.2 Phase boundaries

Phase diagram of a substance : regions of p and T at which its various phases are thermodynamically stable (see Fig. 4.1)

Phase boundary : the line separating the regions where two phases coexist in equilibrium

Vapour pressure : the pressure of a vapour in equilibrium with a liquid (in solid : sublimation vapour pressure)

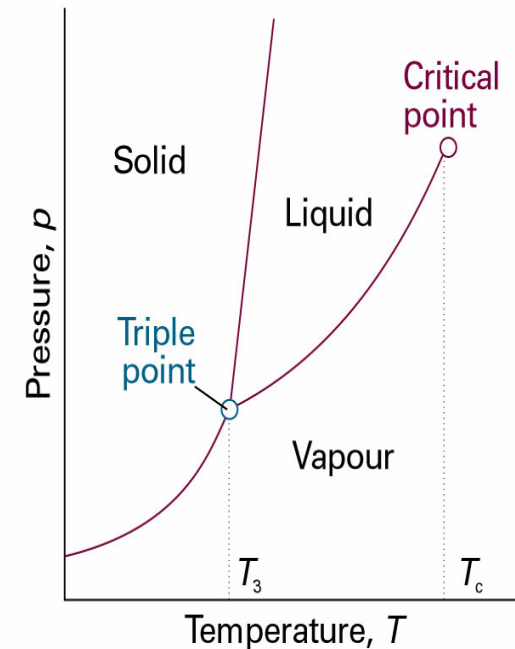


Fig. 4.1 The general regions of pressure and temperature where solid, liquid, or gas is stable (that is, has minimum molar Gibbs energy) are shown on this phase diagram. For example, the solid phase is the most stable phase at low temperatures and high pressures. In the following paragraphs we locate the precise boundaries between the regions.



4.2 Phase boundaries

(a) Critical points and boiling points

Boiling : free vaporization throughout the liquid

Boiling temperature : T at $p_{vap} = p_{ext}$

If $p_{ext} = 1 \text{ atm}$: normal boiling point

$= 1 \text{ bar}$: standard boiling point (1.00 bar = 0.987 atm)

When a liquid is heated in a closed vessel, boiling does not occur.

Instead, as T increases, a continuous $p_{vap} \uparrow$ (i.e., $\rho_{vap} \downarrow$) & a slight $\rho_{liq} \downarrow$

Critical temperature, T_c : temperature at which the interface disappears,

where $\rho_{vap} = \rho_{liq}$

Critical pressure, p_c : vapour pressure at T_c

Supercritical fluid : a single uniform phase at and above T_c (no interface)

(b) Melting points and triple points

Melting (or freezing) temperature : T at which solid and liquid coexist in equilibrium

Normal and standard freezing (or melting) point : freezing (or melting) temperature at 1 atm and 1 bar, respectively

Triple point : a point at which the solid/liquid/gas phase boundaries meet (All three phases simultaneously coexist in equilibrium)

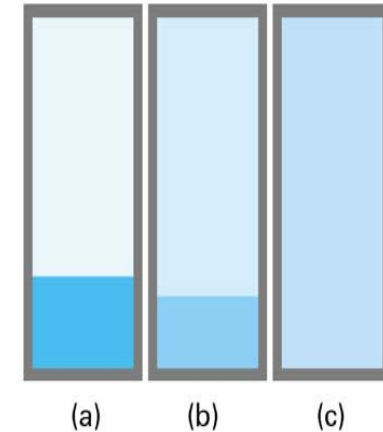


Fig. 4.3 (a) A liquid in equilibrium with its vapour. (b) When a liquid is heated in a sealed container, the density of the vapour phase increases and that of the liquid decreases slightly. There comes a stage, (c), at which the two densities are equal and the interface between the fluids disappears. This disappearance occurs at the critical temperature. The container needs to be strong: the critical temperature of water is 374°C and the vapour pressure is then 218 atm.



4.3 Three typical phase diagrams

(a) Carbon dioxide

Slope of the solid-liquid boundary is positive

- The melting temperature rises as the pressure is increased.

Triple point lies above 1atm

- The liquid cannot exist at normal atmospheric pressures whatever the temperature.
- The solid sublimes when left in the open. (“dry ice”)
- $p > 5.11$ atm: solid \rightarrow liquid

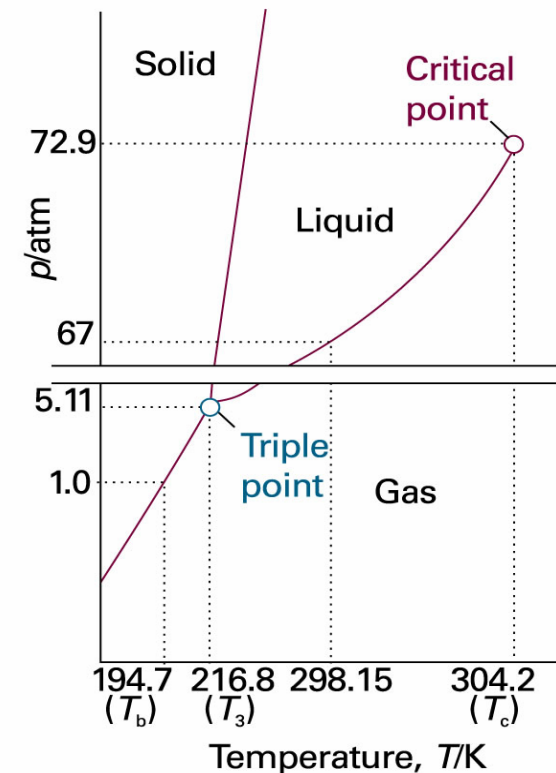


Fig. 4.4 The experimental phase diagram for carbon dioxide. Note that, as the triple point lies at pressures well above atmospheric, liquid carbon dioxide does not exist under normal conditions (a pressure of at least 5.11 atm must be applied).



4.3 Three typical phase diagrams

(b) Water

Liquid-vapour boundary shows

- how p_{vap} of liquid(water) varies with T
- how the boiling T varies with p

Solid-liquid boundary shows

- how T_m varies with p
- steep negative slope (up to ~ 2 kbar) : $p \uparrow \rightarrow T_m \downarrow$

Ice \rightarrow Water

: very open molecular structure of ice partially collapses on melting ($\rho_{liq} > \rho_{sol}$)

At high p ,

- some solid phases

(Ice II, III, V, VI, and VII: polymorphs)

melt at high T

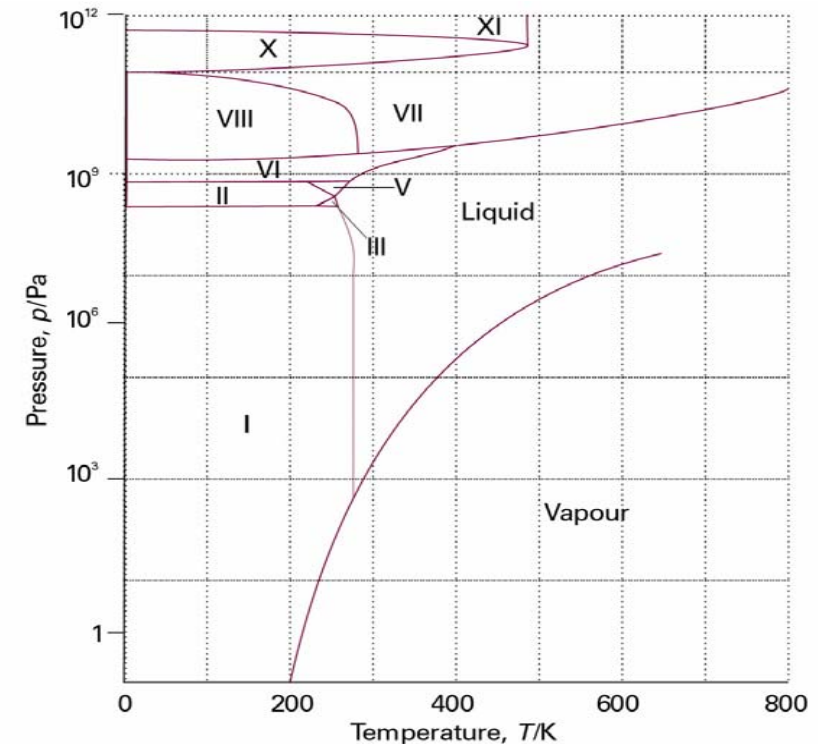


Fig. 4.5 The experimental phase diagram for water showing the different solid phases.

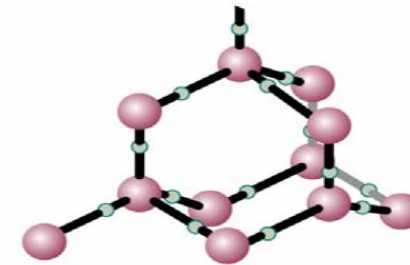


Fig. 4.6 A fragment of the structure of ice (ice-I). Each O atom is linked by two covalent bonds to H atoms and by two hydrogen bonds to a neighbouring O atom, in a tetrahedral array.



4.3 Three typical phase diagrams

(c) Helium

- Solid He can be obtained by holding the atoms together by applying p

- At low T , two isotopes (by mass and spin)

→ ^3He : nucleus of zero spin

$$S_{liq} < S_{sol}$$

melting is exothermic

→ ^4He : nucleus of nonzero spin

λ -line (liq-liq phase transition)

He-I (normal liquid)

He-II (superfluid) :

it flows without viscosity

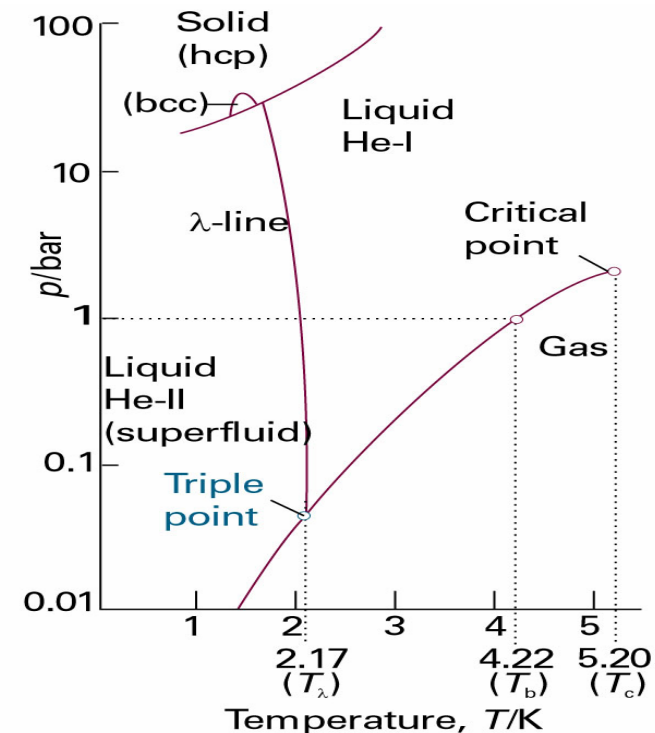


Fig. 4.7 The phase diagram for helium (^4He). The λ -line marks the conditions under which the two liquid phases are in equilibrium. Helium-II is the superfluid phase. Note that a pressure of over 20 bar must be exerted before solid helium can be obtained. The labels hcp and bcc denote different solid phases in which the atoms pack together differently: hcp denotes hexagonal closed packing and bcc denotes body-centred cubic (see Section 20.1 for a description of these structures).



Phase stability and phase transitions

4.4 The thermodynamics criterion of equilibrium

Chemical potential, μ

- Molar Gibbs energy in a one-component system ($\mu = G_m$)
- *At equilibrium, μ of a substance is the same throughout a sample regardless of how many phases are present.*

(from the 2nd law of thermodynamics)

If dn of the substance is transferred (location 1 \rightarrow location 2),

- Change of $G \rightarrow -\mu_1 dn$ in location 1 and $\mu_2 dn$ in location 2
- Overall change : $dG = (\mu_2 - \mu_1)dn$
- If $\mu_1 > \mu_2$: spontaneous change, if $\mu_1 = \mu_2$
: no change (equilibrium)

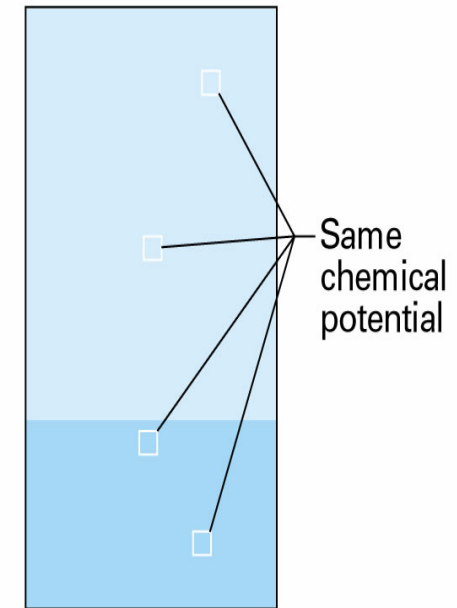


Fig. 4.8 When two or more phases are in equilibrium, the chemical potential of a substance (and, in a mixture, a component) is the same in each phase and is the same at all points in each phase.



4.5 The dependence of stability on the conditions

(a) The temperature dependence of phase stability

The variation of the chemical potential with T for a pure substance

$$\therefore \left(\frac{\partial \mu}{\partial T} \right)_p = -S_m \quad \text{As } T \uparrow, \mu \downarrow \text{ (a negative slope of } \mu \text{ vs } T \text{)} \\ \text{and then } S_m > 0$$

Normally, $S_m(g) > S_m(l) > S_m(s)$, (see Fig 4.9)

As $T \uparrow$, the stable phase (solid \rightarrow liquid \rightarrow gas)

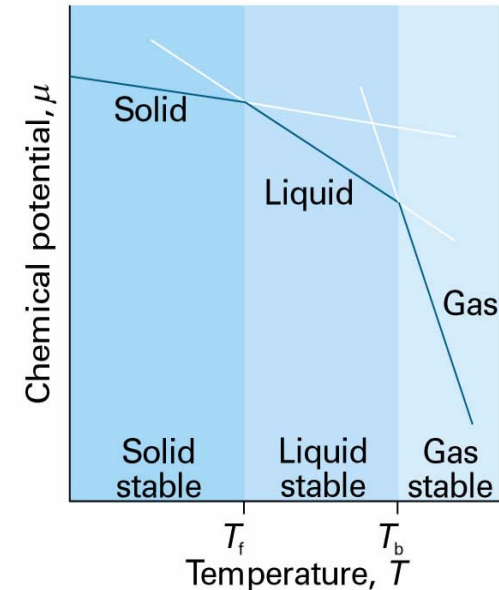


Fig. 4.9 The schematic temperature dependence of the chemical potential of the solid, liquid, and gas phases of a substance (in practice, the lines are curved). The phase with the lowest chemical potential at a specified temperature is the most stable one at that temperature. The transition temperatures, the melting and boiling temperatures (T_f and T_b , respectively), are the temperatures at which the chemical potentials of the two phases are equal.



4.5 The dependence of stability on the conditions

(b) The response of melting to applied pressure

The variation of the chemical potential with p : $\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$

As $p \uparrow$, $\Delta \mu(l) > \Delta \mu(s)$ ($\because V_m(l) > V_m(s)$) & $T_f \uparrow$

[but, in case of water: $\Delta \mu(s) > \Delta \mu(l)$ & $T_f \downarrow$]

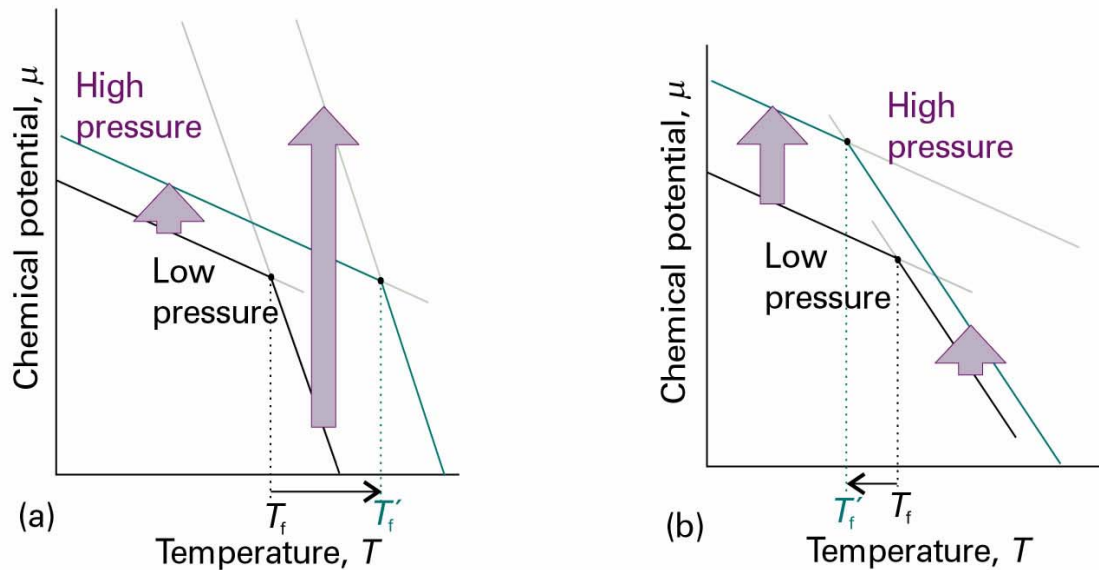


Fig. 4.10 The pressure dependence of the chemical potential of a substance depends on the molar volume of the phase. The lines show schematically the effect of increasing pressure on the chemical potential of the solid and liquid phases (in practice, the lines are curved), and the corresponding effects on the freezing temperatures. (a) In this case the molar volume of the solid is smaller than that of the liquid and $\mu(s)$ increases less than $\mu(l)$. As a result, the freezing temperature rises. (b) Here the molar volume is greater for the solid than the liquid (as for water), $\mu(s)$ increases more strongly than $\mu(l)$, and the freezing temperature is lowered.

4.5 The dependence of stability on the conditions

(c) The effect of applied pressure on vapour pressure

When p is applied to a condensed phase, $p_{vap} \uparrow$

If the condensed phase is liquid,

- the pressurizing gas might dissolve and change the properties of liquid
- gas solvation (the attachment of molecules from liquid to gas)

When Δp is applied, $p = p^* e^{V_m \Delta P / RT}$ (p^* : normal vapor pressure)

If $V_m \Delta P / RT \ll 1$, $p \approx p^* \left(1 + \frac{V_m \Delta P}{RT} \right)$ or $\frac{p - p^*}{p^*} \approx \frac{V_m \Delta P}{RT}$

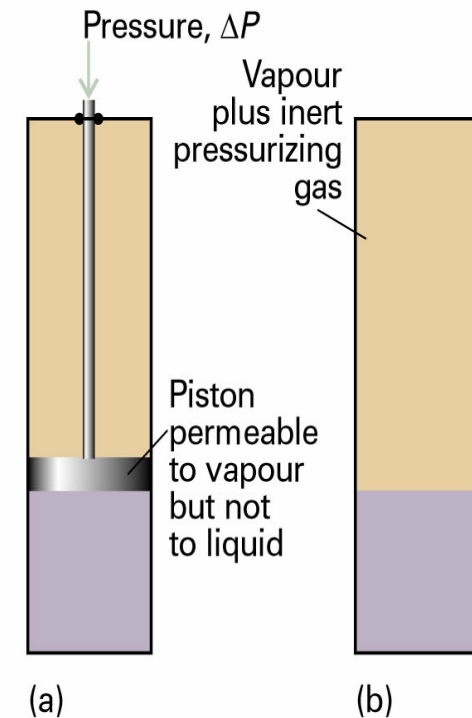


Fig. 4.11 Pressure may be applied to a condensed phases either (a) by compressing the condensed phase or (b) by subjecting it to an inert pressurizing gas. When pressure is applied, the vapour pressure of the condensed phase increases.



4.5 The dependence of stability on the conditions

Justification 4.1 The vapour pressure of a pressurized liquid

Since $d\mu(g) = V_m(g)dp$ and $V_m(g) = RT/p$ for a perfect gas,

$$d\mu(g) = \frac{RTdp}{p}$$

$$\frac{RTdp}{p} = V_m(l)dp \quad \text{because } \mu(g) = \mu(l) \text{ at equilibrium, and } d\mu(l) = V_m(l) dp$$

$$p(l): p \rightarrow p^* + \Delta p,$$

$$RT \int_{p^*}^p \frac{dp}{p} = \int_{p^*}^{p^* + \Delta p} V_m(l) dP \quad \longrightarrow \quad \boxed{\ln \frac{p}{p^*} = \frac{V_m(l)}{RT} \Delta P}$$



4.5 The dependence of stability on the conditions

Illustration 4.1

For water, which has density 0.997g/cm^3 at 25°C and therefore molar volume $18.1\text{cm}^3/\text{mol}$, when the pressure is increased by 10 bar (that is, $\Delta P = 1.0 \times 10^5 \text{ Pa}$)

$$\frac{V_m(l)\Delta P}{RT} = \frac{(1.81 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}) \times (1.0 \times 10^6 \text{ Pa})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = \frac{1.81 \times 1.0 \times 10}{8.3145 \times 298}$$

where we have used $1\text{J} = 1\text{Pa}\cdot\text{m}^3$. It follows that $p = 1.0073p^*$, an increase of 0.73 percent.



4.6 The location of phase boundaries

Where the phases α and β are in equilibrium, $\mu_\alpha(p, T) = \mu_\beta(p, T)$

(a) The slopes of the phase boundaries

Let p and T be changed infinitesimally,
but the two phases of α and β remain in equilibrium.

From $dG = Vdp - SdT$,

$$d\mu = V_m dp - S_m dT, \quad (d\mu_\alpha = d\mu_\beta)$$

$$-S_{\alpha,m} dT + V_{\alpha,m} dp = -S_{\beta,m} dT + V_{\beta,m} dp$$

$$(V_{\beta,m} - V_{\alpha,m}) dp = (S_{\beta,m} - S_{\alpha,m}) dT$$

$$\frac{dp}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V} \quad : \text{ Clapeyron equation}$$

- Exact expression for the slope of the phase boundary and applies to any phase equilibrium of any pure substance
- Using thermodynamic data, the appearance of phase diagrams are predictable.

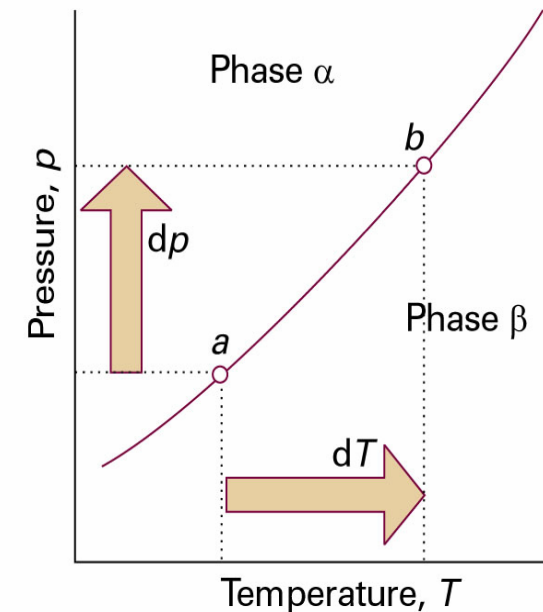


Fig. 4.12 When pressure is applied to a system in which two phases are in equilibrium (at a), the equilibrium is disturbed. It can be restored by changing the temperature, so moving the state of the system to b . It follows that there is a relation between dp and dT that ensures that the system remains in equilibrium as either variable is changed.



4.6 The location of phase boundaries

(b) The solid-liquid boundary

Since the molar entropy of melting at T is $\Delta_{trs}H/T$,

$$\frac{dp}{dT} = \frac{\Delta_{fus}H}{T\Delta_{fus}V} \quad \text{Since } \Delta_{trs}H > 0 \text{ (except } ^3\text{He)} \text{ and } \Delta_{trs}V > 0 \text{ (but small),}$$

$dp/dT > 0$ with a steep slope

If T_m is T^* at p^* and T at p ,

$$\int_{p^*}^p dp = \frac{\Delta_{fus}H}{\Delta_{fus}V} \int_{T^*}^T \frac{dT}{T} \quad \longrightarrow \quad p \approx p^* + \frac{\Delta_{fus}H}{\Delta_{fus}V} \ln \frac{T}{T^*}$$

By using $\ln \frac{T}{T^*} = \ln \left(1 + \frac{T - T^*}{T^*} \right) \approx \frac{T - T^*}{T^*}$

Therefore, $p \approx p^* + \frac{\Delta_{fus}H}{T^* \Delta_{fus}V} (T - T^*)$ (See Fig. 4. 13)

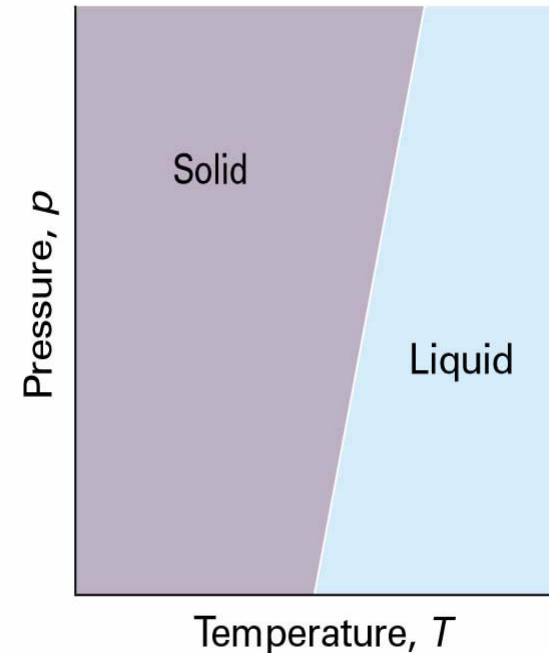


Fig. 4.13 A typical solid–liquid phase boundary slopes steeply upwards. This slope implies that, as the pressure is raised, the melting temperature rises. Most substances behave in this way.



4.6 The location of phase boundaries

(c) The liquid-vapour boundary

Since S_{vap} at T is equal to $\Delta_{vap}H/T$,

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V}$$

Since $\Delta_{vap}H > 0$ (except ^3He) and $\Delta_{vap}V > 0$ (a large change in volume)
 $dp/dT > 0$, much smaller slope than s/l boundary

Because $\Delta_{vap}V = V_m(g) - V_m(l) \approx V_m(g)$ and
 $V_m(g) = RT/p$ for a perfect gas,

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T(RT/p)} \rightarrow \frac{d \ln p}{dT} = \frac{\Delta_{vap}H}{RT^2} \quad : \text{ Clausius-Clapeyron equation}$$

If $\Delta_{vap}H$ is independent of T ,

$$p = p^* e^{-\chi}, \quad \chi = \frac{\Delta_{vap}H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \rightarrow \text{plotted curve in Fig. 4.14}$$

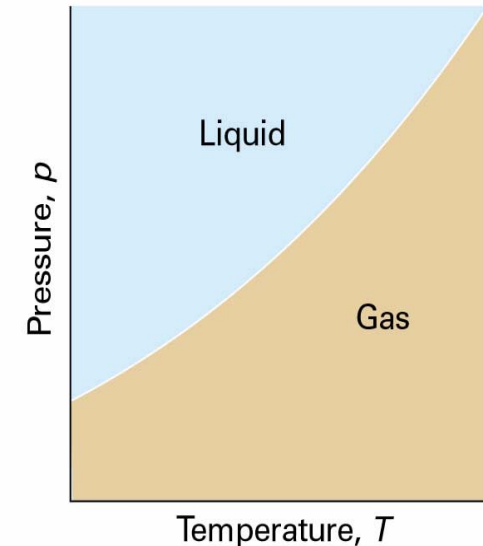


Fig. 4.14 A typical liquid–vapour phase boundary. The boundary can be regarded as a plot of the vapour pressure against the temperature. Note that, in some depictions of phase diagrams in which a logarithmic pressure scale is used, the phase boundary has the opposite curvature (see Fig. 4.7). This phase boundary terminates at the critical point (not shown).



4.6 The location of phase boundaries

Illustration 4.2

Because the normal boiling point of benzene is 80°C (353K) and $\Delta_{\text{vap}}H^\circ = 30.8\text{kJmol}^{-1}$, to calculate the vapour pressure at 20°C (293K), we write

$$\chi = \frac{3.08 \times 10^4 \text{ Jmol}^{-1}}{8.3145 \text{ JK}^{-1}\text{mol}^{-1}} \left(\frac{1}{293 \text{ K}} - \frac{1}{353 \text{ K}} \right) = \frac{3.08 \times 10^4}{8.3145} \left(\frac{1}{293} - \frac{1}{353} \right)$$

and substitute this value into $p=p^*e^{-\chi}$ with $p^*=101\text{kPa}$.

The result is 12kPa .

The experimental value is 10kPa .

(d) The solid-vapour boundary

Replace $\Delta_{\text{vap}}H$ by $\Delta_{\text{sub}}H$

$\Delta_{\text{sub}}H > \Delta_{\text{vap}}H$: steeper slope than l/v

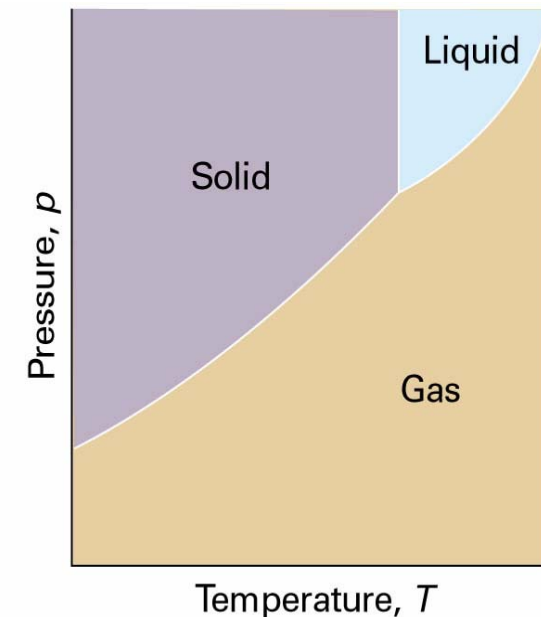


Fig. 4.15 Near the point where they coincide (at the triple point), the solid–gas boundary has a steeper slope than the liquid–gas boundary because the enthalpy of sublimation is greater than the enthalpy of vaporization and the temperatures that occur in the Clausius–Clapeyron equation for the slope have similar values.



4.7 The Ehrenfest classification of phase transitions

Ehrenfest classification : the classification scheme of phase transitions proposed by Paul Ehrenfest

$\alpha \rightarrow \beta$ transition :

$$\left(\frac{\partial \mu_\beta}{\partial p}\right)_T - \left(\frac{\partial \mu_\alpha}{\partial p}\right)_T = V_{\beta,m} - V_{\alpha,m} = \Delta_{trs} V \quad \left(\frac{\partial \mu_\beta}{\partial T}\right)_p - \left(\frac{\partial \mu_\alpha}{\partial T}\right)_p = -S_{\beta,m} + S_{\alpha,m} = \Delta_{trs} S = \frac{\Delta_{trs} H}{T_{trs}}$$

Since $\Delta_{trs} V, \Delta_{trs} H \neq 0$ for melting and vaporization, the first derivatives of μ with p and T are discontinuous at the transition.

First-order phase transition

- 1st derivative of μ with T is discontinuous (See Fig. 4.16a)
- $C_p (= dH/dT \text{ at const } p) \rightarrow \infty$ at T_{trs} - ex) boiling of water

Second-order phase transition

- 1st derivative of μ with T is continuous, but 2nd derivative is discontinuous (see Fig. 4.16b)
(V_m and S_m do not change at transition)
- C_p is discontinuous but does not become infinite at T_{trs}
ex) conducting-superconducting transition in metals at low T

λ -transition

- not first-order but C_p becomes infinite at T_{trs}
- plot looks like λ (the Greek letter) (See Fig. 4.17)
ex) order/disorder transition in alloy, onset of ferromagnetism, and fluid/superfluid (L_{He})



4.7 The Ehrenfest classification of phase transitions

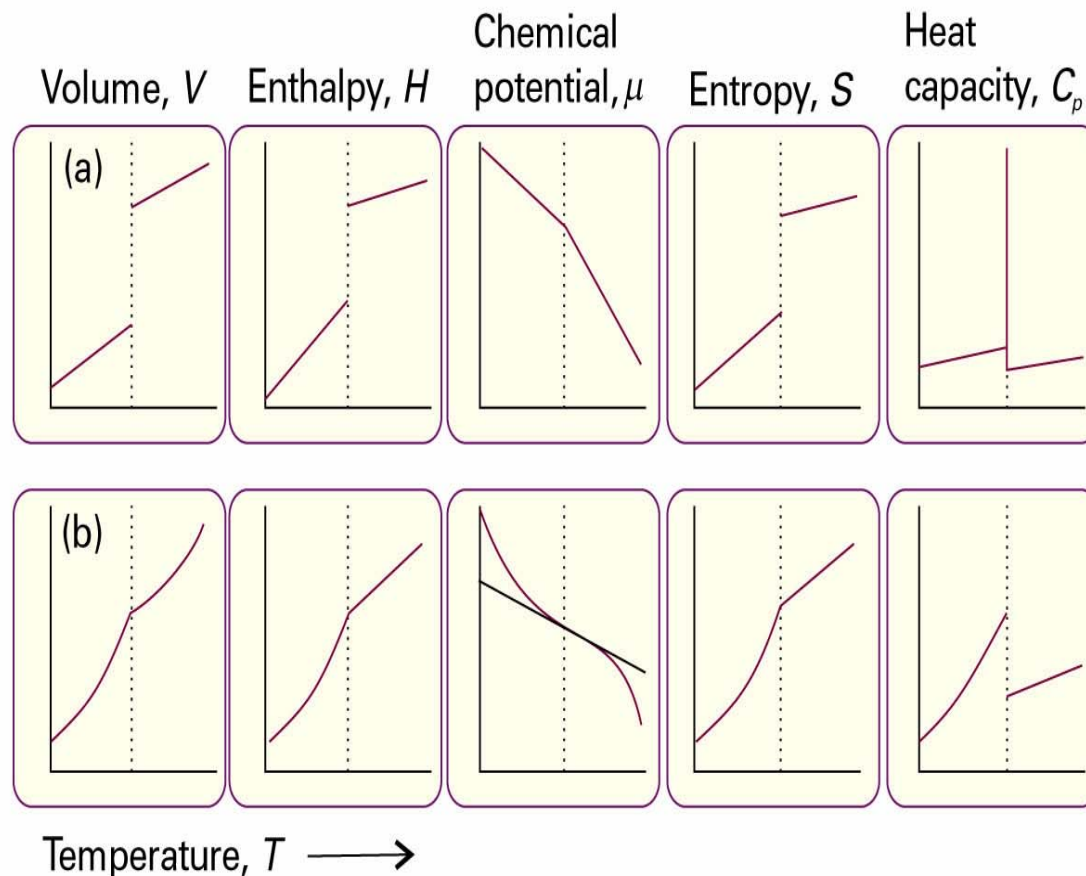


Fig. 4.16 The changes in thermodynamic properties accompanying (a) first-order and (b) second-order phase transitions.

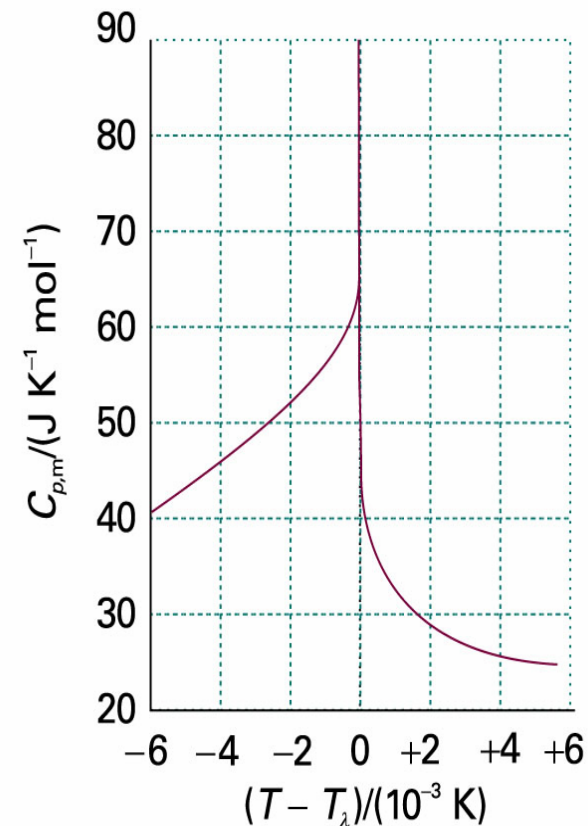


Fig. 4.17 The λ -curve for helium, where the heat capacity rises to infinity. The shape of this curve is the origin of the name λ -transition.



4.7 The Ehrenfest classification of phase transitions

Molecular interpretation 4.1

second-order transition

ex) a change in symmetry of the crystal structure of a solid
tetragonal ($a=b \neq c$) \rightarrow cubic at the transition (See Fig. 4.18)

Above T_{trs} , all three directions will expand equally

λ -transition

ex) β -brass (CuZn)

low $T \rightarrow$ orderly array of alternating Cu and Zn atoms (See Fig. 4.19)

high $T (\geq 742 \text{ K}) \rightarrow$ random array of atoms (islands growth)

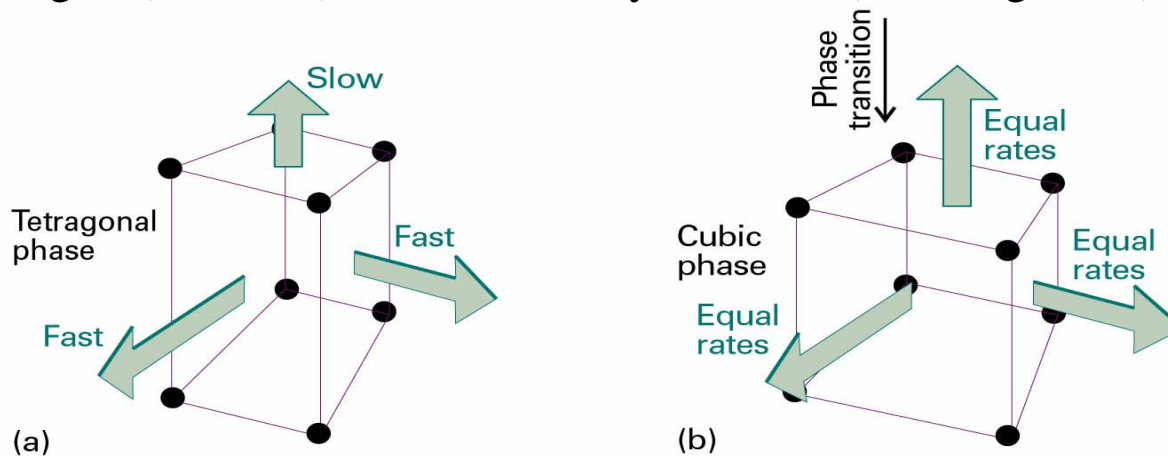


Fig. 4.18 One version of a second-order phase transition in which (a) a tetragonal phase expands more rapidly in two directions than a third, and hence becomes a cubic phase, which (b) expands uniformly in three directions as the temperature is raised. There is no rearrangement of atoms at the transition temperature, and hence no enthalpy of transition.

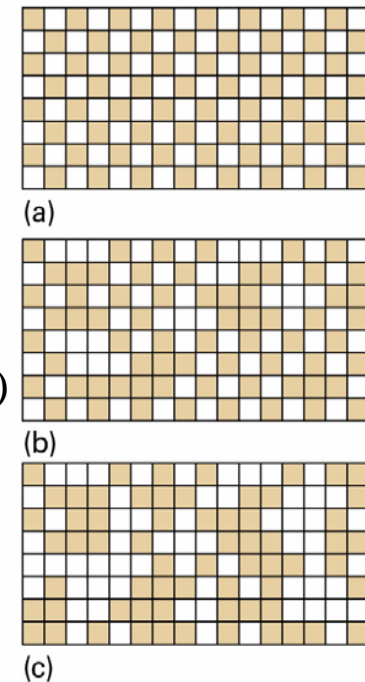


Fig. 4.19 An order–disorder transition. (a) At $T = 0$, there is perfect order, with different kinds of atoms occupying alternate sites. (b) As the temperature is increased, atoms exchange locations and islands of each kind of atom form in regions of the solid. Some of the original order survives. (c) At and above the transition temperature, the islands occur at random throughout the sample.

