Part 1: Equilibrium

6. Physical transformation of pure substances

Bilingual Program

6. Physical transformation of pure substances

The simplest applications of thermodynamics to chemically significant systems are to the discussion of the phase transitions of pure substances. We shall see that a phase diagram is a map of the pressures and temperatures at which each phase of a substance is the most stable.

6. Physical transformation of pure substances

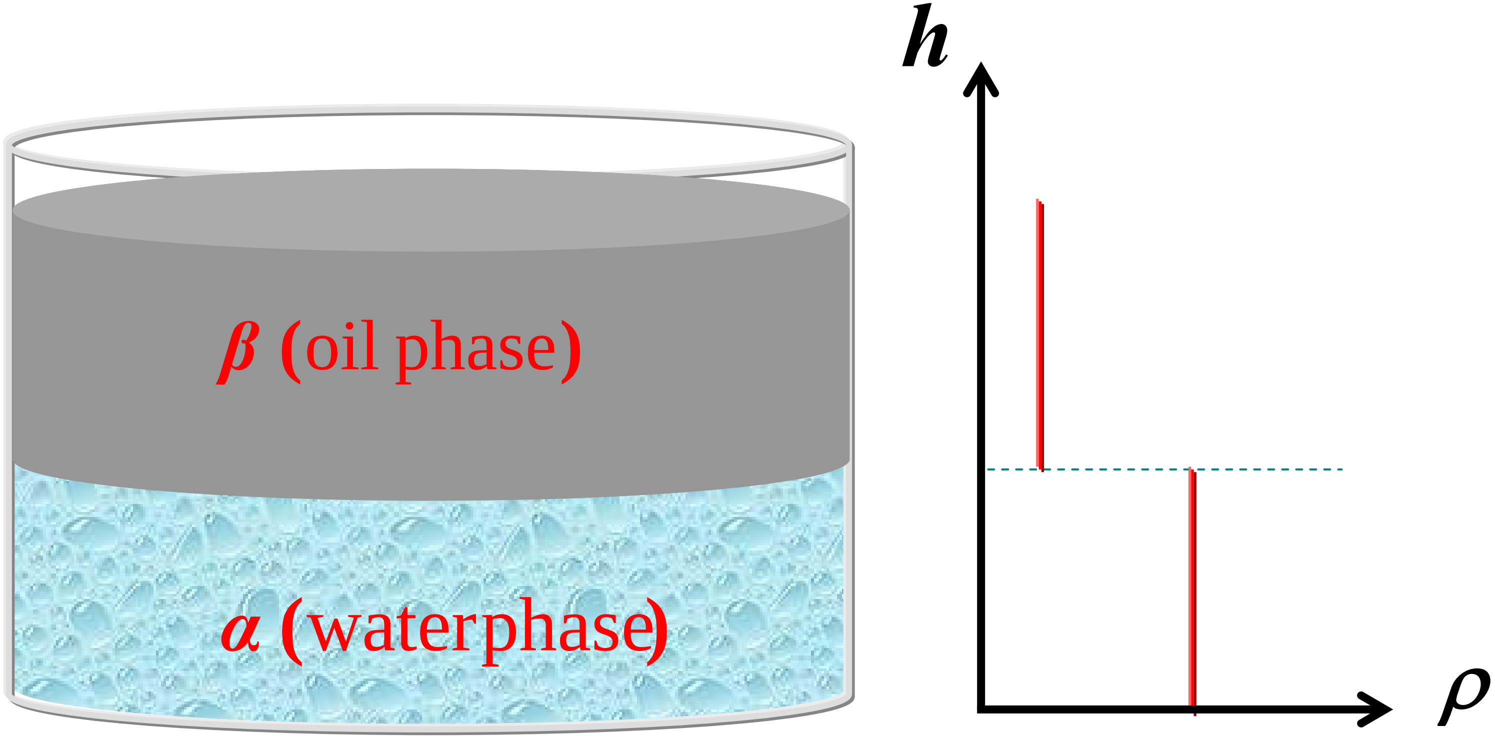
In this chapter, we first describe the interpretation of empirically determined phase diagrams for a selection of materials; then we turn to a consideration of the factors that determine the positions and shapes of the boundaries between the regions on a phase diagram; and finally, we consider the thermodynamic discussion of liquid surfaces, such as surface tension and capillary action.

6. Physical transformation of pure substances

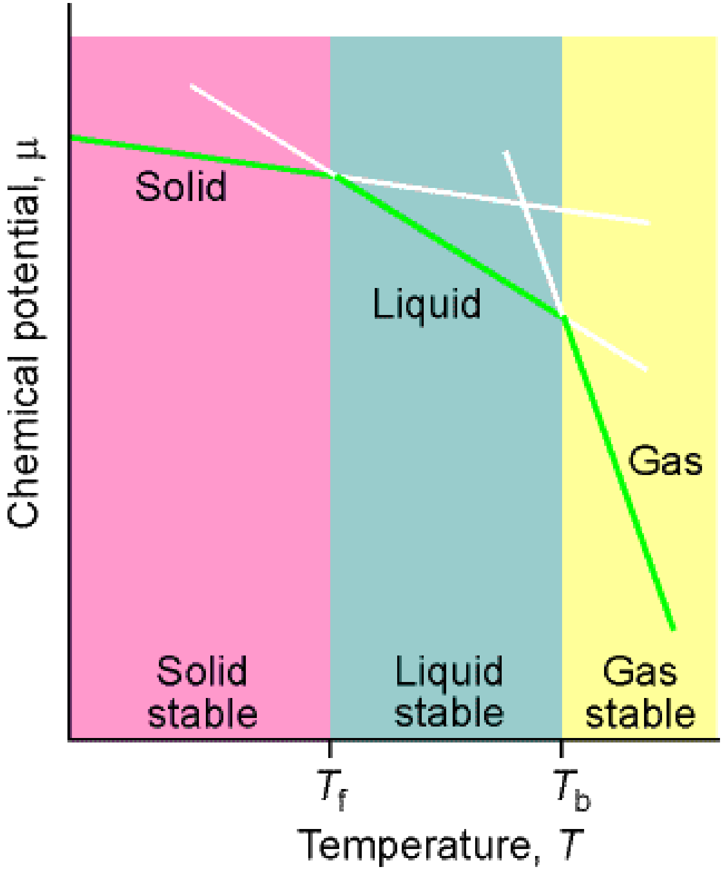
6.1 The stabilities of phases-Basic concepts

1). The phase

A phase of a substance is a form of matter that is uniform throughout in chemical composition and physical state.



6.1 The stabilities of phases-Basic concepts



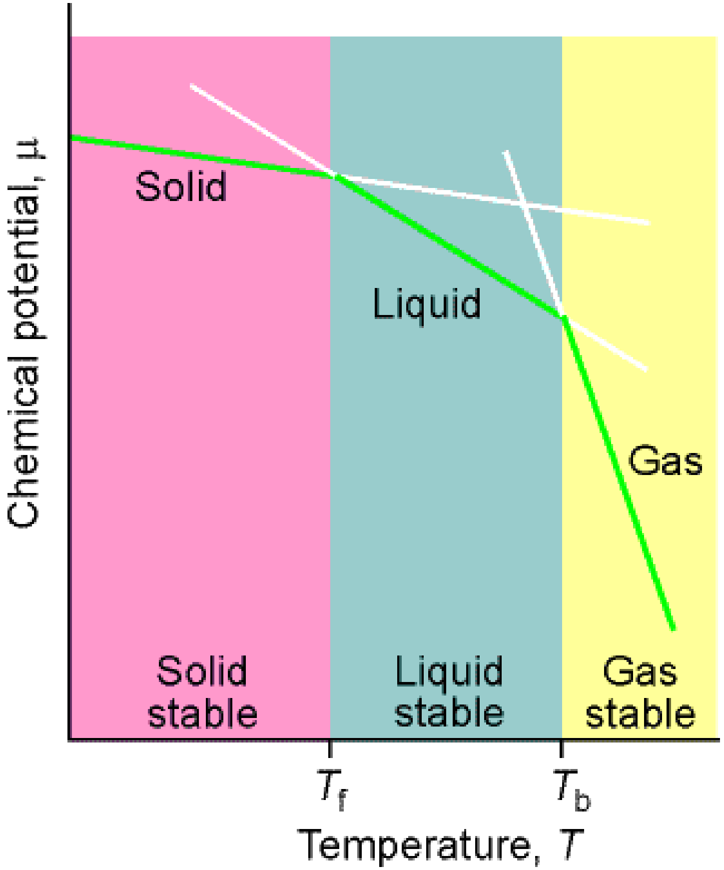
The schematic *T* dependence of the chemical potential of the solid, liquid, and gas phases of a substance

2). The phase transition

A phase transition is the spontaneous conversion of one phase into another phase, occurs at the specific temperature for a given pressure.

e.g. at 1 atm, ice is the stable phase below 0℃, but above 0 ℃ liquid water is the stable phase.

6.1 The stabilities of phases−Basic concepts



The schematic T dependence of the chemical potential of the solid, liquid, and gas phases of a substance

3). T_{trs}

A transition temperature, T_{trs}, represents the temperature at which the two chemical potentials are equal and the two phases are in equilibrium at the specific pressure.

Note that the normal transition temperature of p =1.0 atm

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Phase diagrams

6.1 The stabilities of phases

6.2 Phase boundaries ▶

6.3 Three typical phase diagrams

Phase stability and phase transitions

6.4 The thermodynamic criterion of equilibrium

6.5 The dependence of stability on the conditions

6.6 The location of phase boundaries

6.7 The Ehrenfest classification of phase transitions

The physical liquid surface

6.8 Surface tension

6.9 Curved surfaces

6.10 Capillary action

6.2 Phase boundaries

Phase equilibrium for one component system

$$\text{The solid phase} \xleftrightarrow[\text{freezing}]{\text{melting}} \text{The liquid phase}$$

$$\text{The solid phase } (\alpha) \xleftrightarrow[\text{transition}]{\text{phase(s)}} \text{The solid phase } (\beta)$$

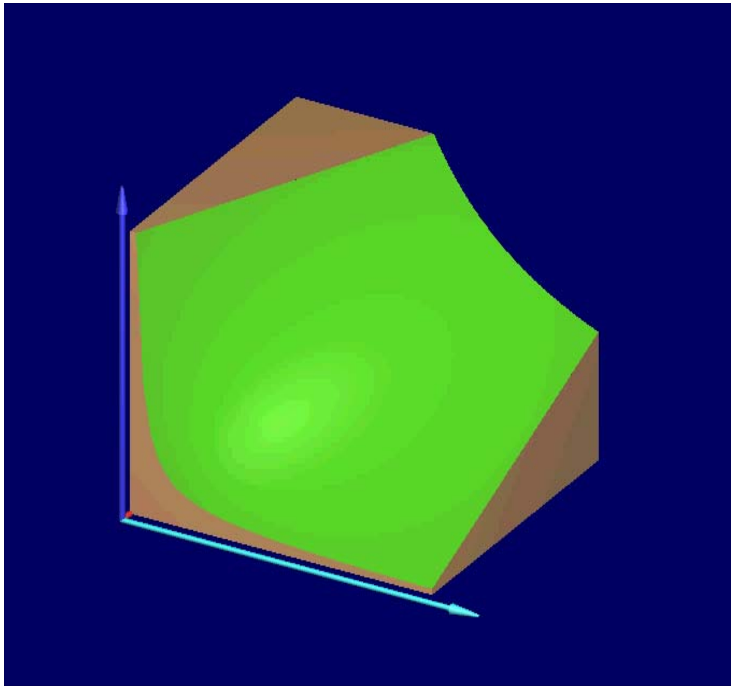
$$\text{The liquid phase} \xleftrightarrow[\text{condensing}]{\text{vaporizing}} \text{The vapour phase}$$

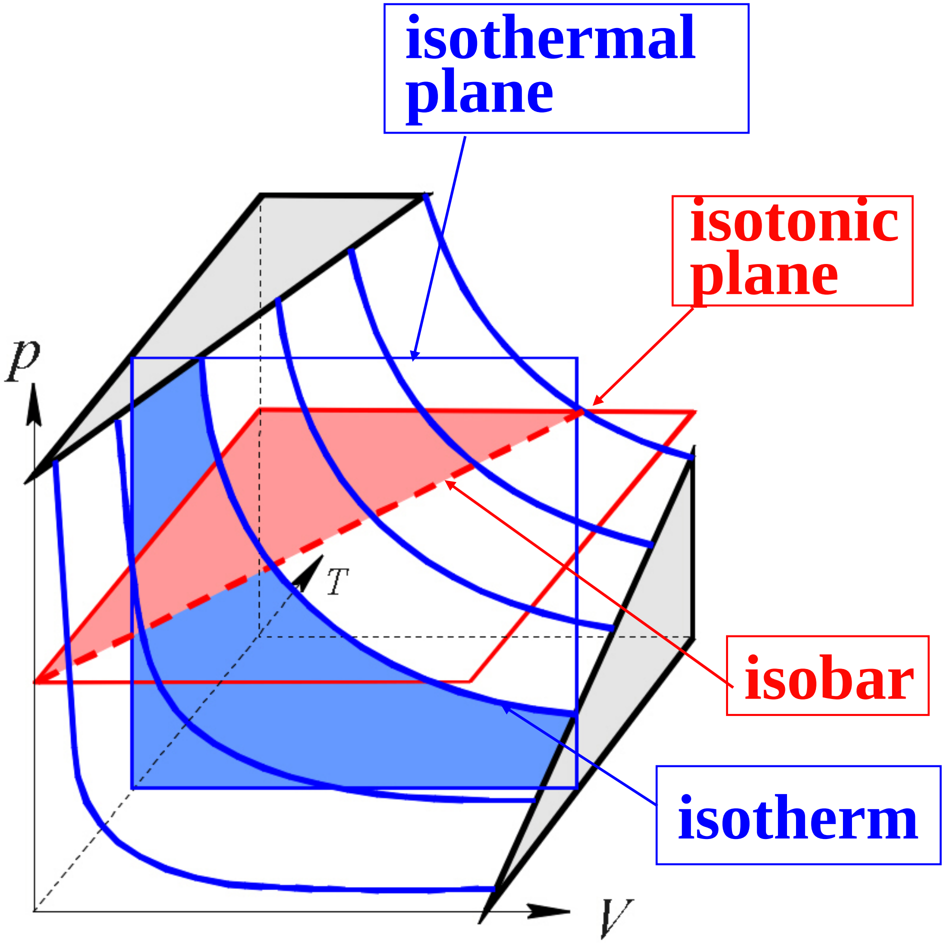
$$\text{The solid phase} \xleftrightarrow[\text{condensing}]{\text{sublimation}} \text{The vapour phase}$$

$$\text{The solid} \longleftrightarrow \text{The liquid} \longleftrightarrow \text{The vapour}$$

6.2 Phase boundaries

1). The *p,V,T* relations − for a perfect gas





isothermal plane

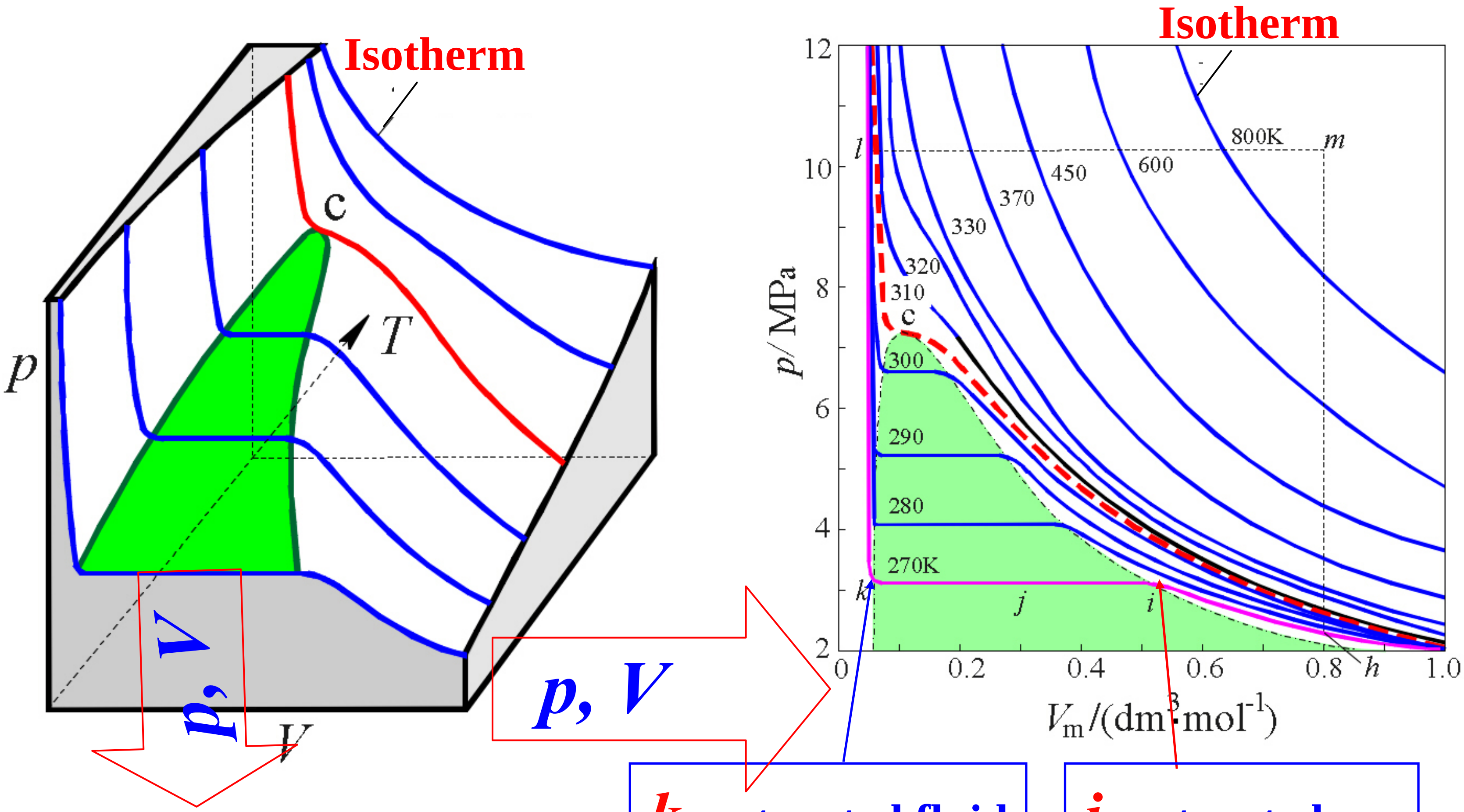
isotonic plane

isobar

isotherm

6.2 Phase boundaries

1). The *p*,*V*,*T* relations– for real fluids

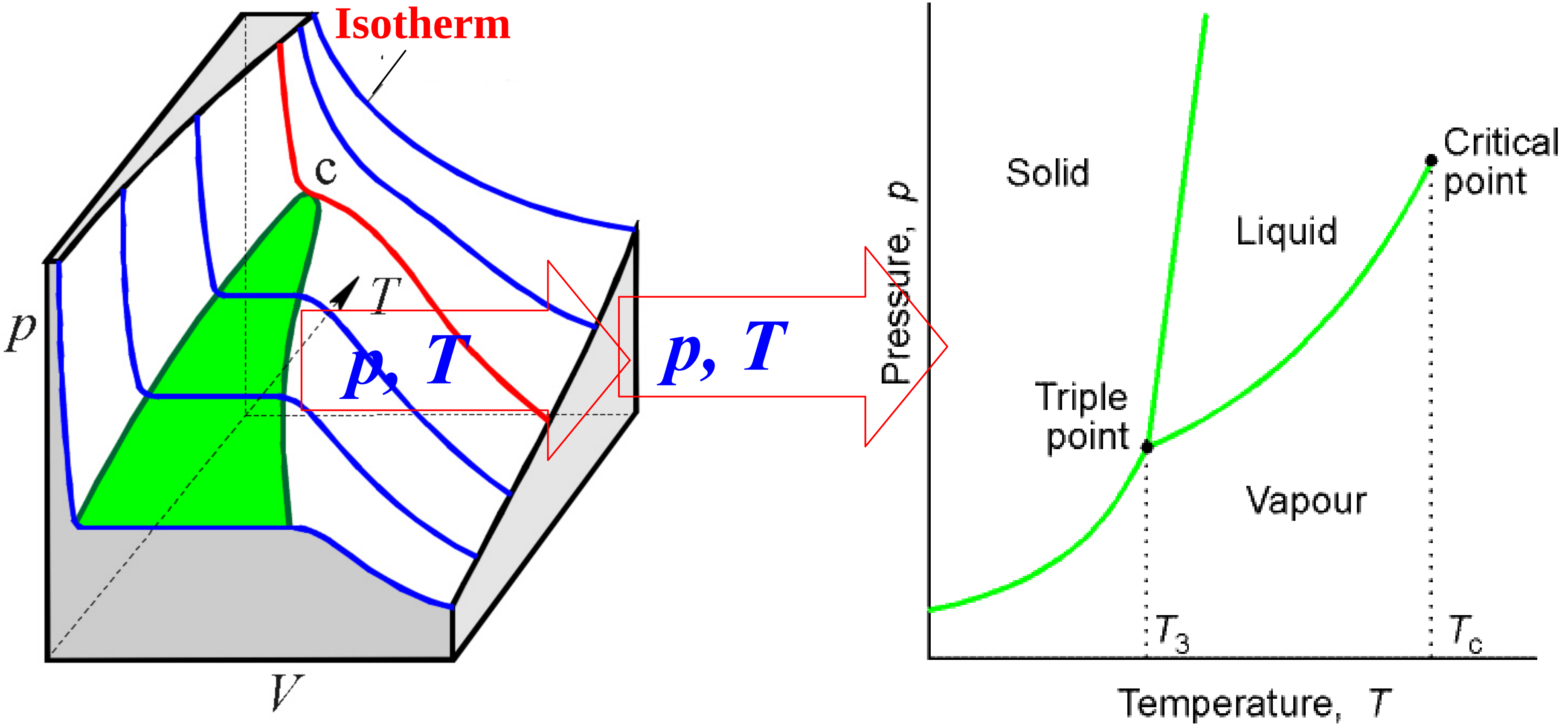


***k*, saturated fluid**

***i*, saturated gas**

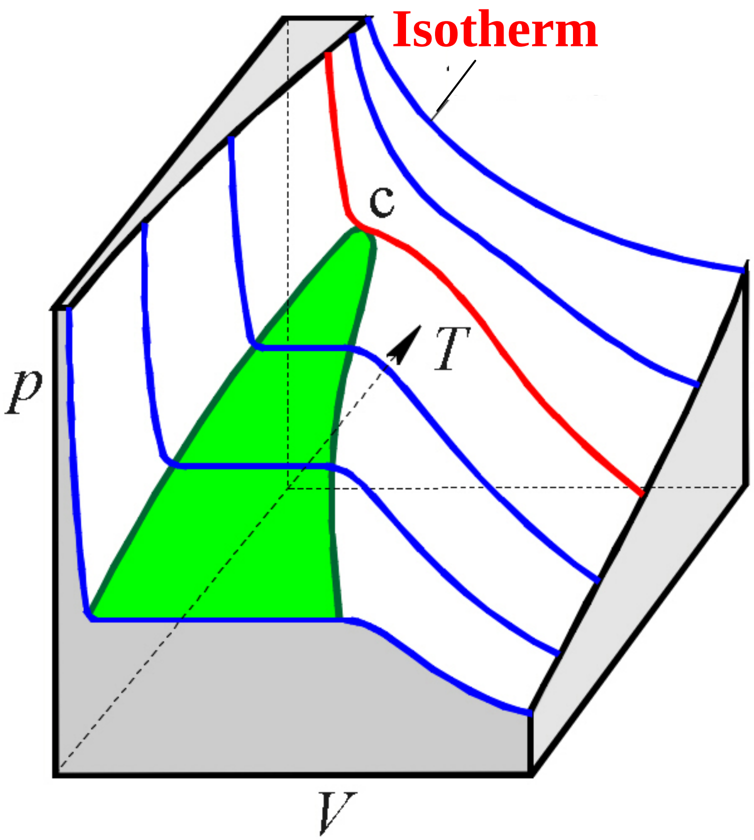
6.2 Phase boundaries

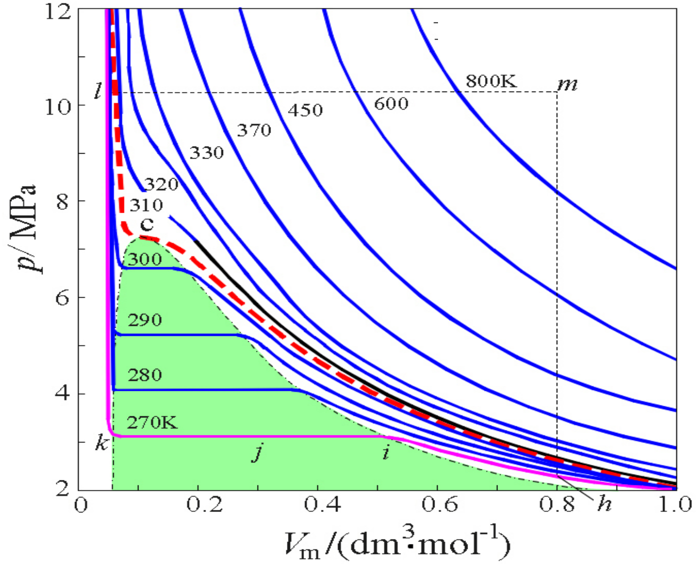
1). The *p*,*V*,*T* relations– for real fluids

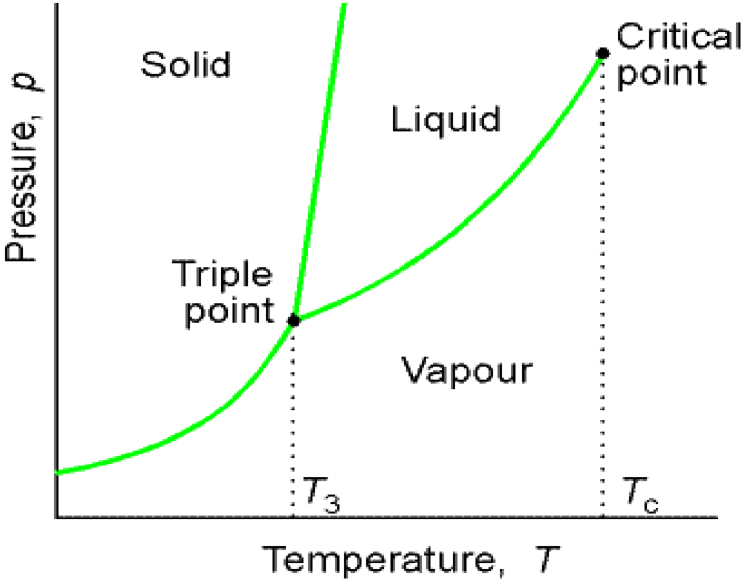


6.2 Phase boundaries

1). The *p*,*V*,*T* relations

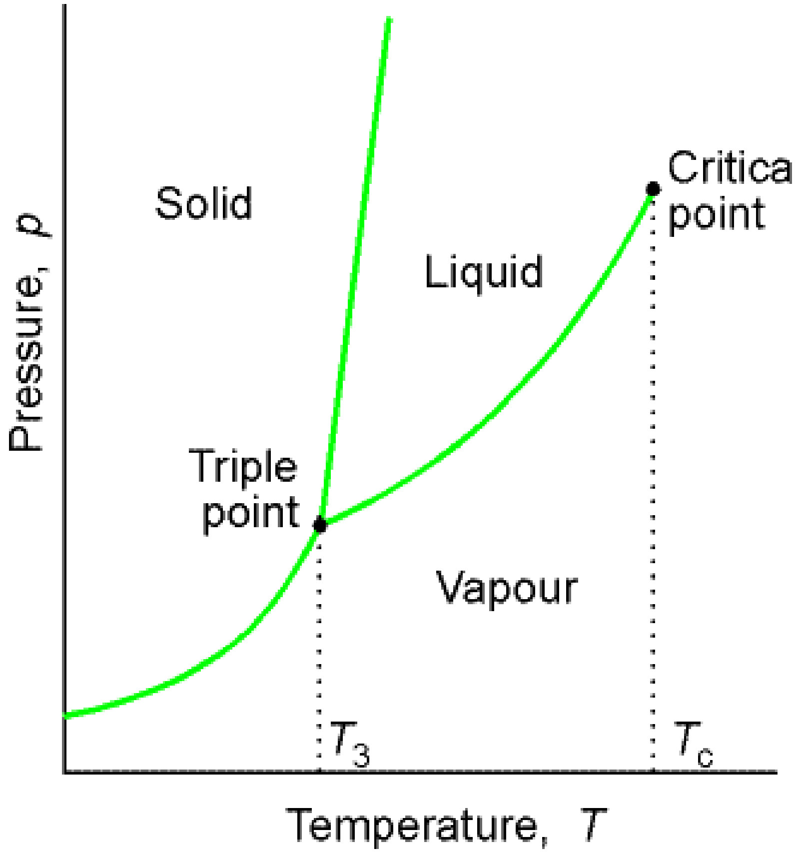






6.2 Phase boundaries

2). The phase diagram



The phase diagram

The phase boundaries

The lines separating the regions are called phase boundaries; these lines show the values of p and T at which two phases coexist in equilibrium

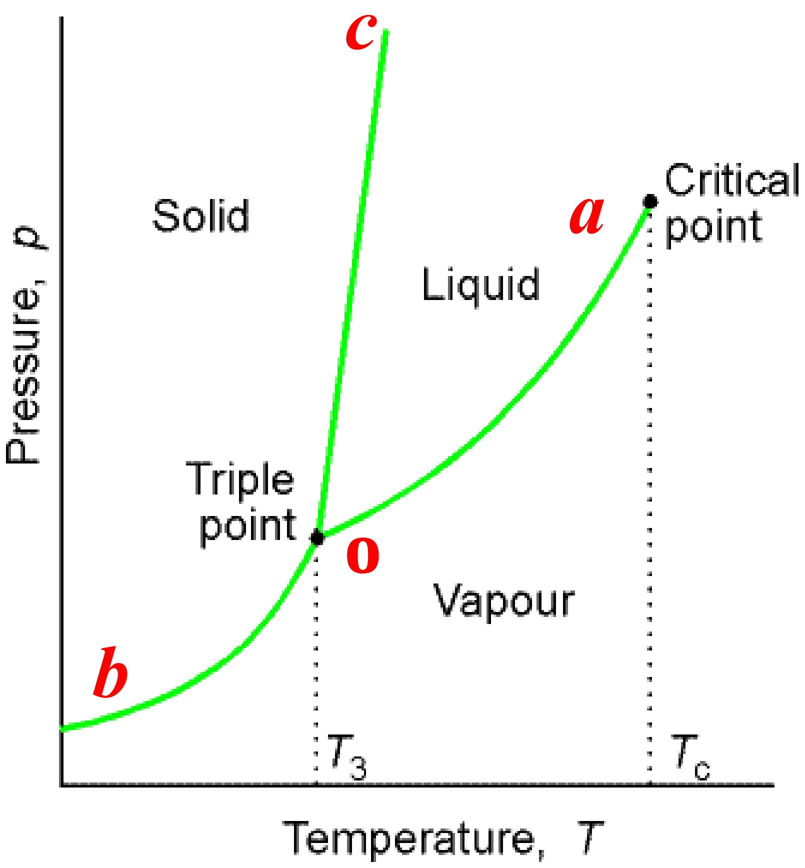
The liquid-vapour phase boundary;

The liquid-solid phase boundary;

The solid-vapour phase boundary.

6.2 Phase boundaries

2). The phase diagram



The line o −*a*

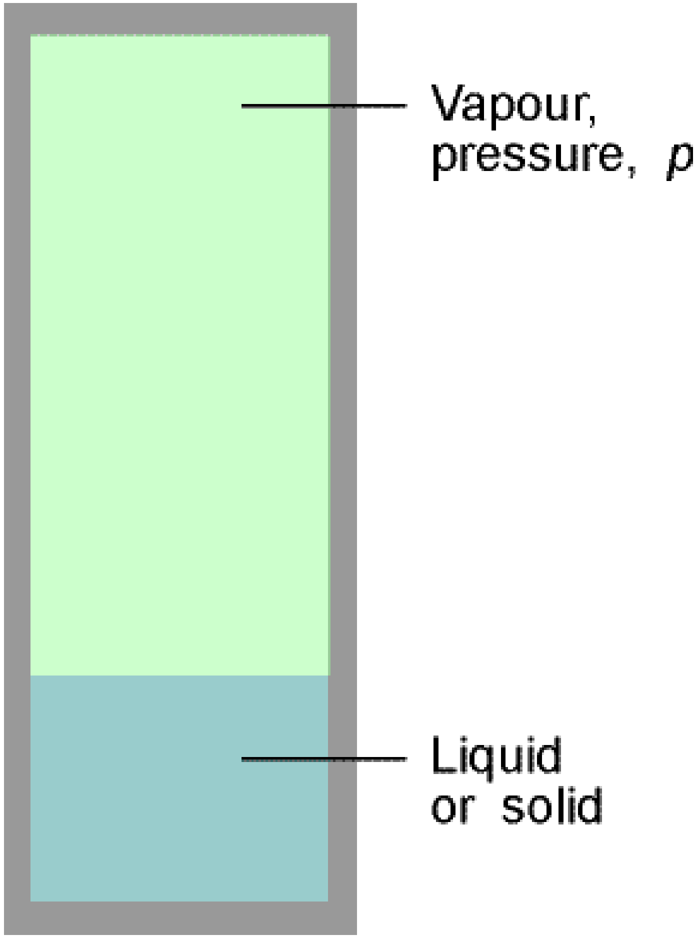
The line o −*b*

The line o −*c*

The triple point o

6.2 Phase boundaries

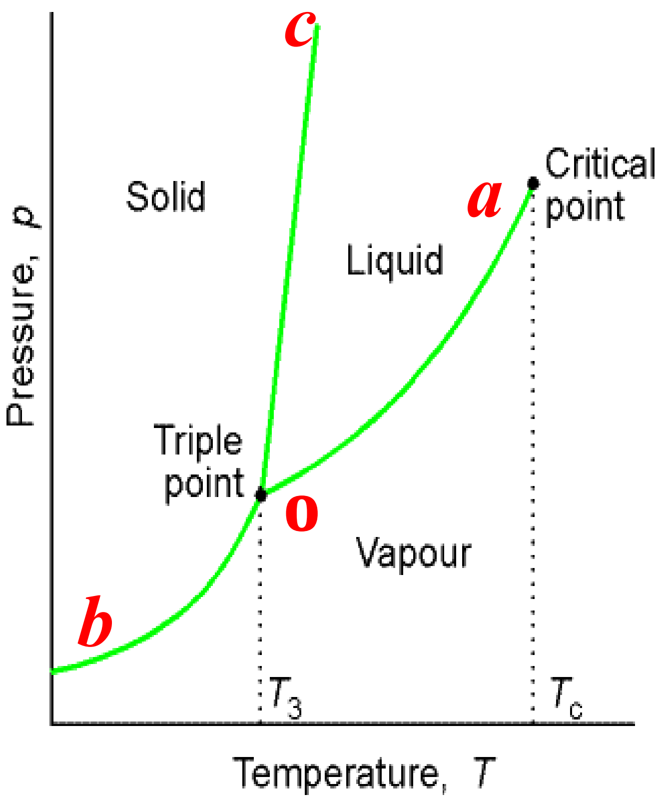
3). Boiling points



The vapour pressure of a liquid or solid is the pressure exerted by the vapour in equilibrium with the condensed phase.

6.2 Phase boundaries

3). Boiling points



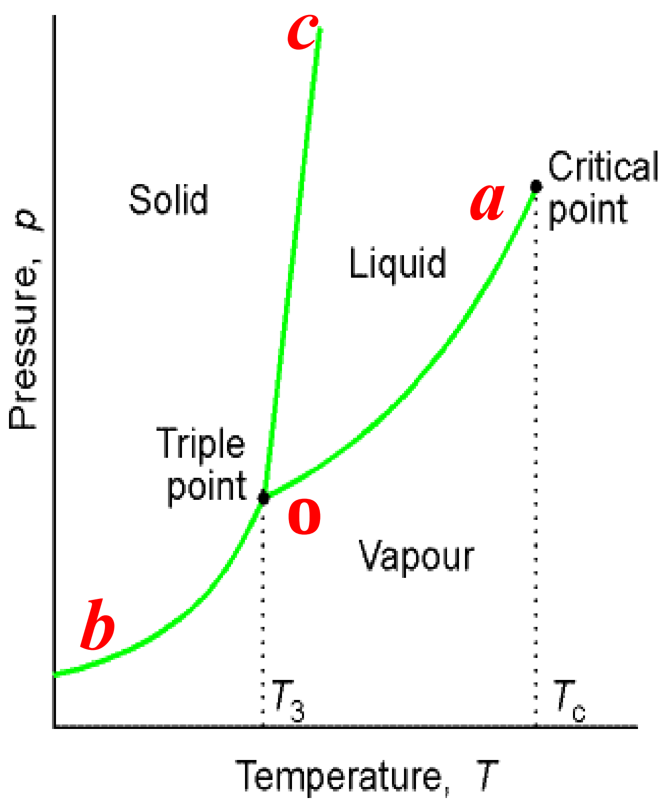
The phase diagram

When a liquid is heated in an open vessel, the liquid vaporizes from its surface. At *T* at which its vapour *p* would be equal to the external *p*, vaporization can occur throughout the bulk of the liquid. The condition of free vaporization throughout the liquid is called boiling.

The normal boiling point, *p*=1 atm
The standard boiling point, *p*=1 bar

6.2 Phase boundaries

4). Critical points



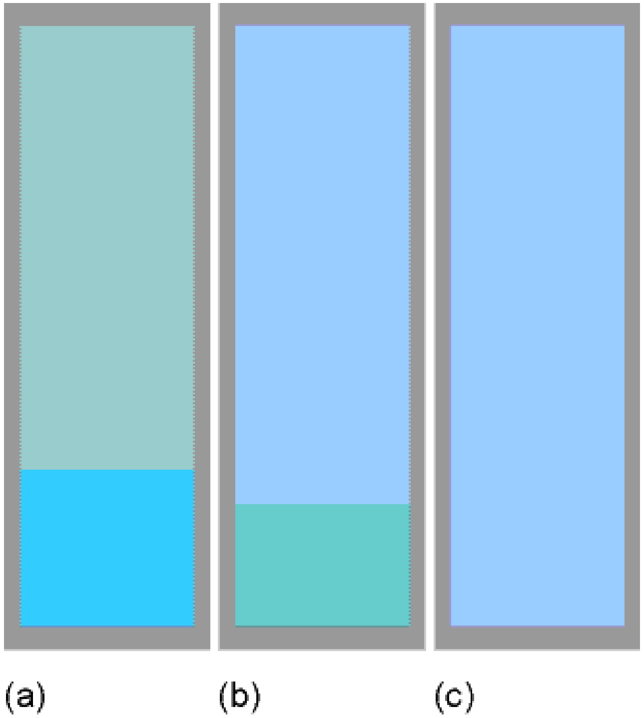
The phase diagram

Boiling does not occur when a liquid is heated in a closed vessel. There comes a stage when the density of the vapour is equal to that of the remaining liquid and the surface between the two phases disappears. The temperature at which the surface disappears is the critical temperature, T_c, of the substance.

At and above T_c, a single uniform phase is called a supercritical fluid. above T_c, the liquid phase of the substance does not exist.

6.2 Phase boundaries

4). Critical points



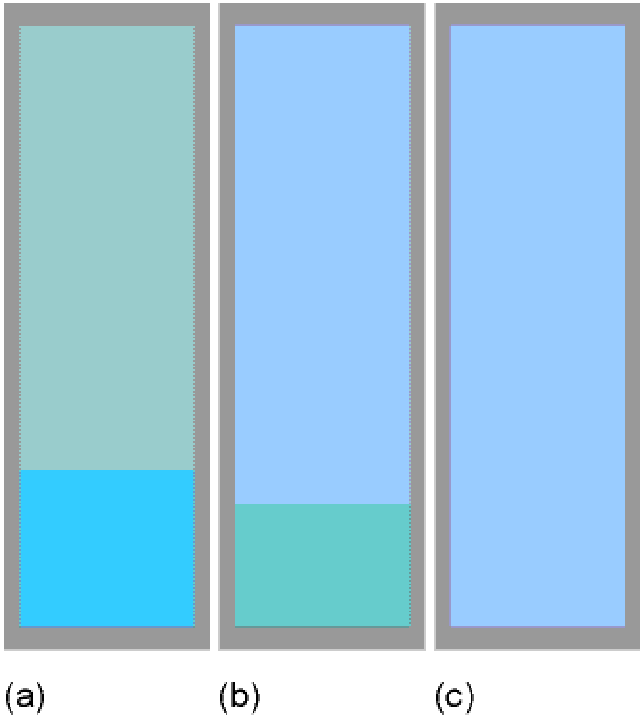
(a)A liquid in equilibrium with its vapour.

(b)When a liquid is heated in a sealed container, the density of the vapour phase increases and that of the liquid decreases slightly.

(c)There comes a stage, at which the two densities are equal and the interface between the fluids disappears.

6.2 Phase boundaries

4). Critical points



This disappearance occurs at the critical temperature. The critical temperature of water is 374°C and the vapour pressure is then 218 atm.

6.2 Phase boundaries

5). Melting and freezing points

The melting freezing temperature: the temperature at which, under a specified pressure, the liquid and solid phases of a substance coexist in equilibrium is called.

The normal melting and freezing point: The temperature when the pressure is 1atm is called the normal melting and freezing point.

The standard melting and freezing point: the melting and freezing point when the pressure is 1 bar.

6.2 Phase boundaries

6). The triple point

There is a set of conditions under which three different phases of a substance all simultaneously coexist in equilibrium. It is represented by the triple point, a point at which the three phase boundaries meet. The temperature at the triple point is denoted T_3. The triple point of a pure substance is outside our control: it occurs at a single definite pressure and temperature characteristic of the substance.

The triple point of water lies at 273.16 K and 611 Pa

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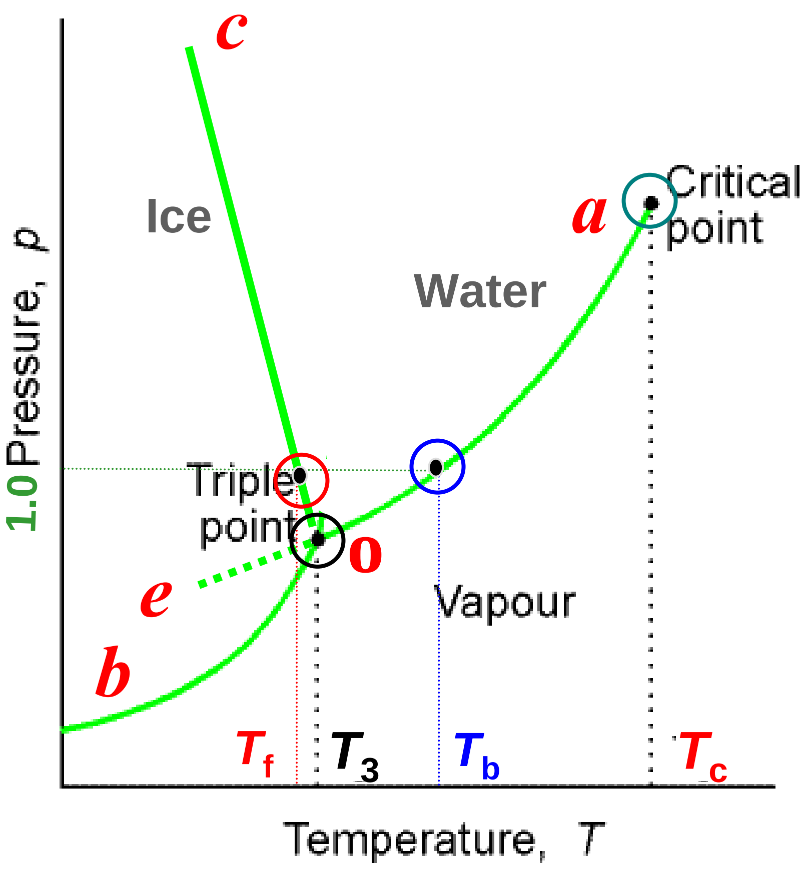
6.3 Three typical phase diagrams

1). Water –low pressure



The phase diagram

Triple point:

T_3=273.16K(p=0.006atm)

Normal freezing point

T_f=273.15K(p=1.0atm)

Normal boiling point

T_b=373.15K(p=1.0atm)

Critical point

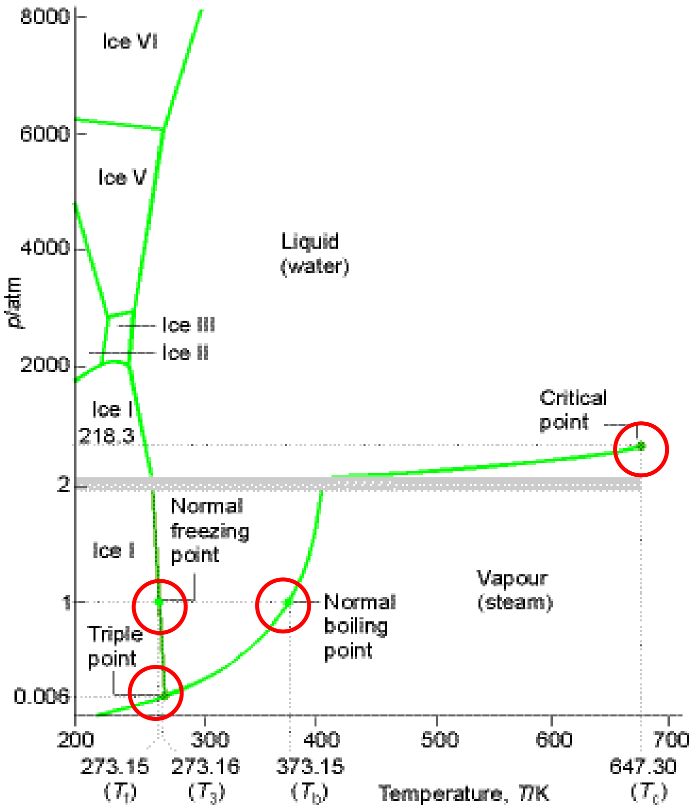
T_c=674.30K(p=218.3atm)

The metastable phase

Thermodynamically unstable phases that persist because the transition is kinetically hindered are called metastable phases.

6.3 Three typical phase diagrams

1). Water-high pressure

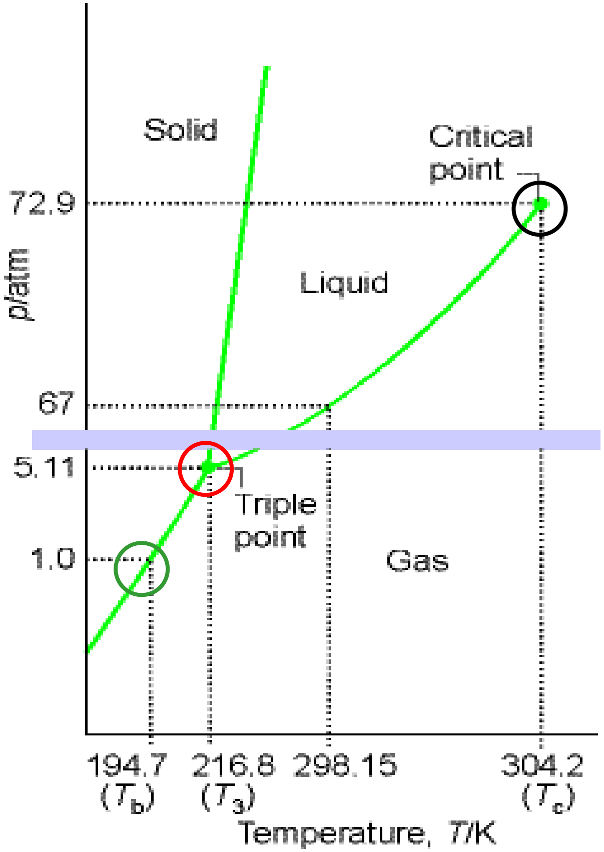


The experimentally determined phase diagram for water

At high pressures, different structural forms of ice come into stability. Some of these phases which are called ice II, III, V, VI, and VII melt at high temperatures. Note that five more triple points occur in the diagram other than the one where vapour, liquid, and ice I coexist. Each one occurs at a definite pressure and temperature that cannot be changed.

6.3 Three typical phase diagrams

2). Carbon dioxide



The experimental phase diagram for carbon dioxide.

Triple point:

T_3=216.8K(p=5.11atm)

Critical point

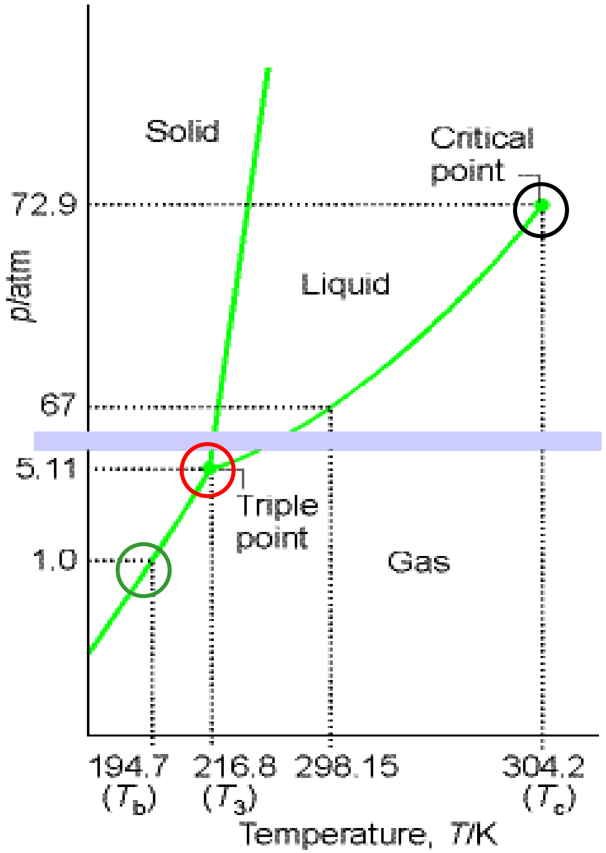
T_c=674.30K(p=72.9atm)

Normal boiling point

T_b=194.7K(p=1.0atm)

6.3 Three typical phase diagrams

2). Carbon dioxide



The experimental phase diagram for carbon dioxide.

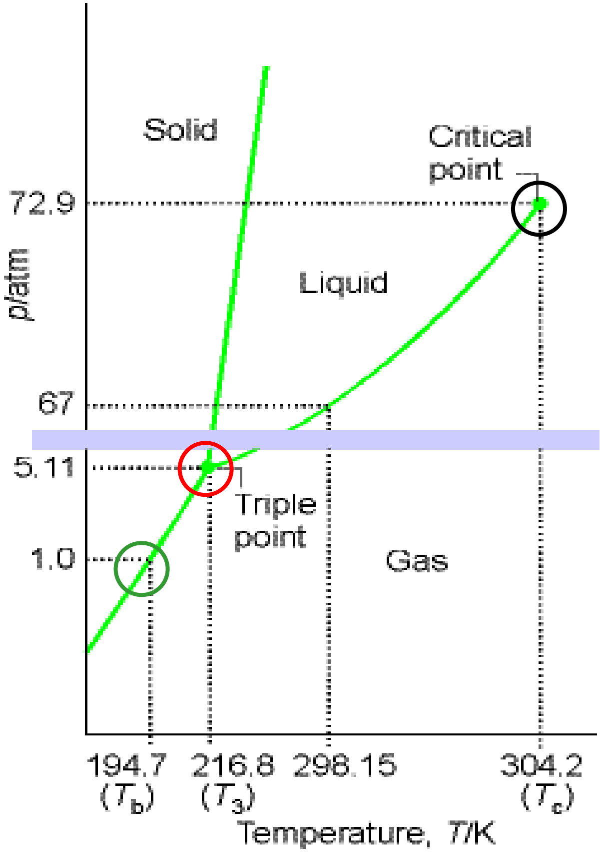
The positive slope of the solid-liquid boundary, which indicates that the melting temperature of solid carbon dioxide rises as the pressure is increased.

The triple point lies above 1 atm, the liquid cannot exist at normal atmospheric pressures whatever the temperature.

The solid sublimes when left in the open - 'dry ice'.

6.3 Three typical phase diagrams

2). Carbon dioxide

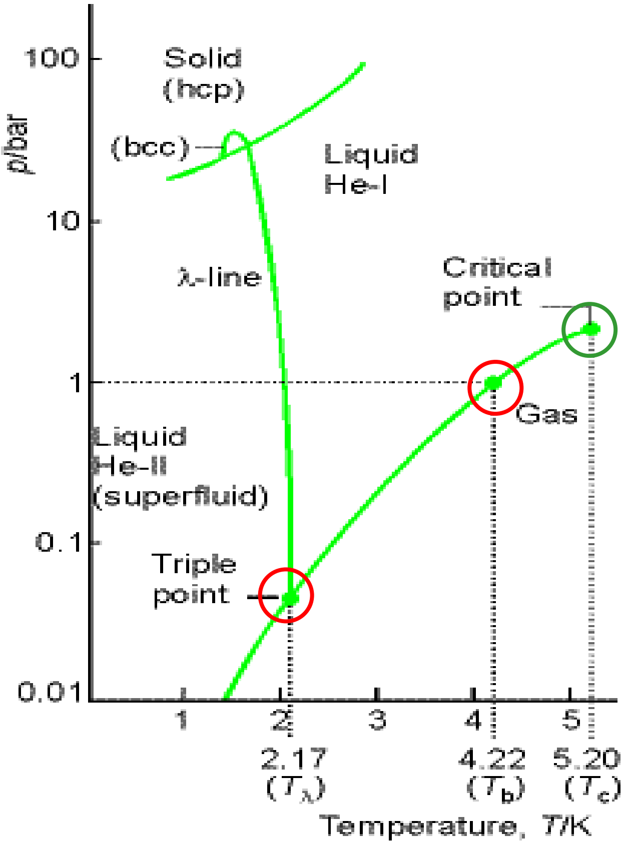


The experimental phase diagram for carbon dioxide.

Supercritical CO_2 (compressed CO_2 above T_c) is used in supercritical fluid chromatography (SFC), a form of chromatography in which the supercritical fluid is used as the mobile phase. A more mundane application of supercritical carbon dioxide is in the extraction.

6.3 Three typical phase diagrams

3). The helium



The phase diagram for ^{4}He

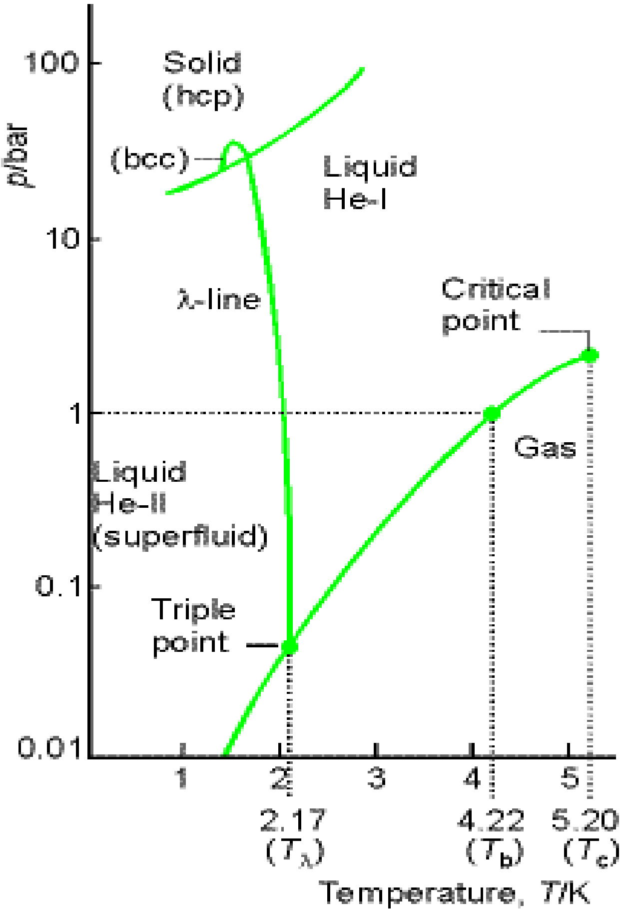
Triple point: T_λ =2.17K

Normal boiling point: T_b=4.22K

Critical point: T_c=674.30K

6.3 Three typical phase diagrams

3). The helium



The phase diagram for helium

Helium behaves unusually at low *T*: the solid and gas phases are never in equilibrium however low the temperature. Solid helium can be obtained only by applying pressure over 20 bar. The pure helium has a liquid-liquid phase transition at its λ -line. The liquid phase marked He-Ⅰ behaves like a normal liquid; the other phase, He-Ⅱ, is a superfluid. It is so called because it flows without viscosity.

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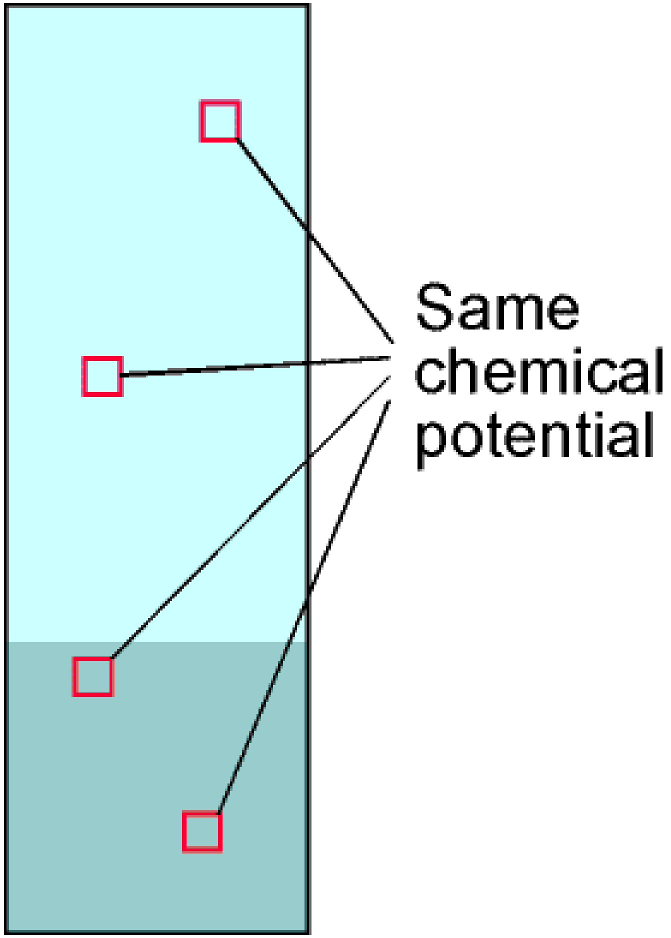
6.4 The thermodynamic criterion of equilibrium

The thermodynamic criterion of equilibrium:

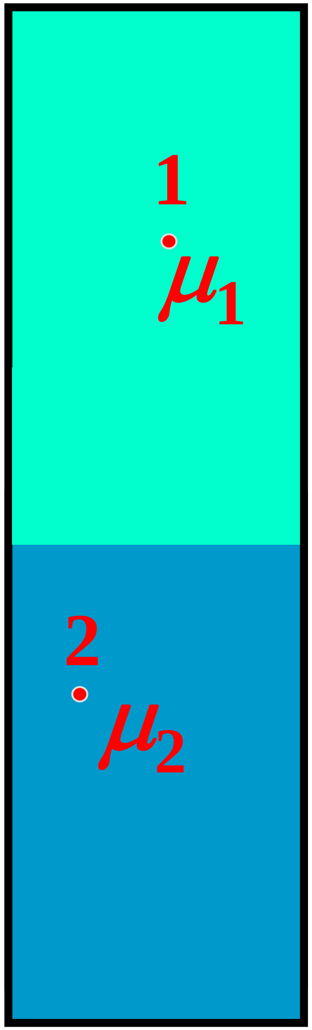
At equilibrium, the chemical potential of a substance is the same throughout a sample, regardless of how many phases are present.

6.4 The thermodynamic criterion of equilibrium



When the liquid and solid phases of a substance are in equilibrium, the chemical potential of the substance is the same throughout the liquid and throughout the solid, and is the same in the solid as in the liquid

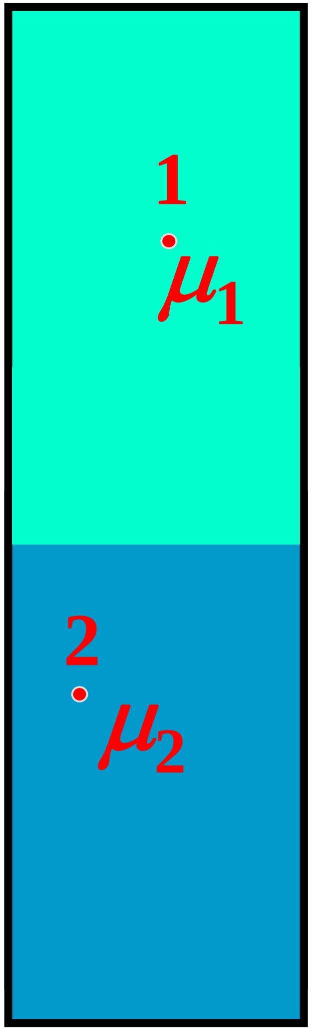
6.4 The thermodynamic criterion of equilibrium



μ_1, at location 1
μ_2, at location 2

When an amount dn of the substance is transferred from one location to the other, the Gibbs energy of the system changes by $-\mu_1$dn when material is removed from location 1, and it changes by + μ_2dn when that material is added to location 2.

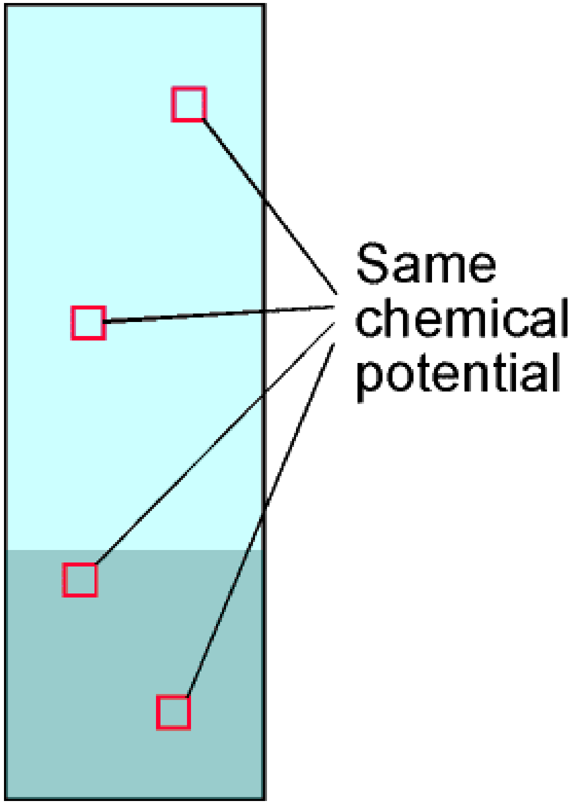
6.4 The thermodynamic criterion of equilibrium



The overall change is therefore $dG = (\mu_2 - \mu_1)dn$. If the chemical potential at location 1 is higher than that at location 2, the transfer is accompanied by a decrease in G, and so has a spontaneous tendency to occur. Only if $\mu_1 = \mu_2$ is there no change in G, and only then is the system at equilibrium.

6.4 The thermodynamic criterion of equilibrium

The thermodynamic criterion of equilibrium



At equilibrium, the chemical potential of a substance is the same throughout a sample, regardless of how many phases are present.

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6.5 The dependence of stability on the conditions

At low *T*, the solid phase of a substance has the lowest chemical potential and, provided the pressure is not too low, is usually the most stable at low *T*.

However, the chemical potentials of phases change with *T* in different ways, and as the temperature is raised the chemical potential of another phase (perhaps another solid phase, a liquid, or a gas) will fall below that of the solid. When that happens, a phase transition occurs if it is kinetically feasible to do so.

6.5 The dependence of stability on the conditions

1) The temperature dependence of phase stability

From $\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T$ **:**

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial p}\right)_T = V$$

$$\left(\frac{\partial G_\mathrm{m}}{\partial T}\right)_p = -S_\mathrm{m} \qquad \mu = \left(\frac{\partial G}{\partial n}\right)_{T,p} = G_\mathrm{m}$$

6.5 The dependence of stability on the conditions

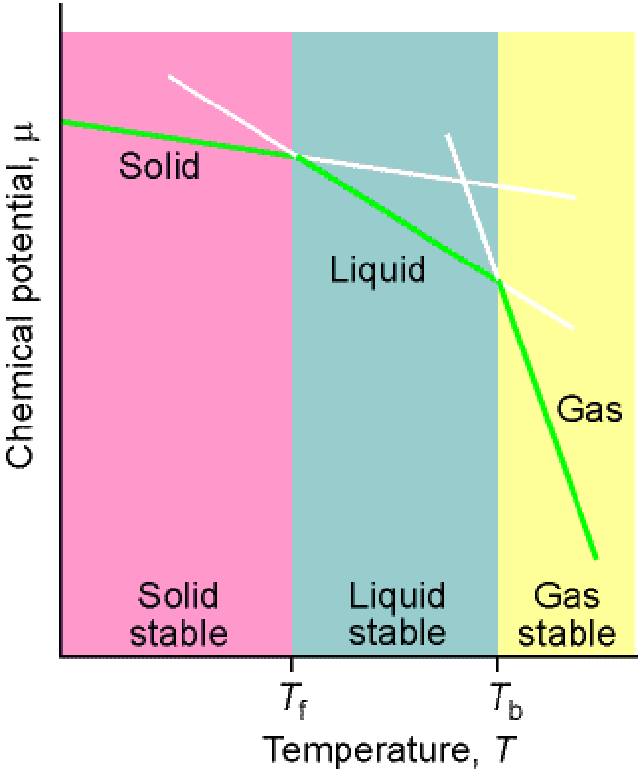
1) The temperature dependence of phase stability

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_{\mathrm{m}}$$

This relation shows that, as the temperature is raised, the chemical potential of a pure substance decreases.

6.5 The dependence of stability on the conditions

1) The temperature dependence of phase stability



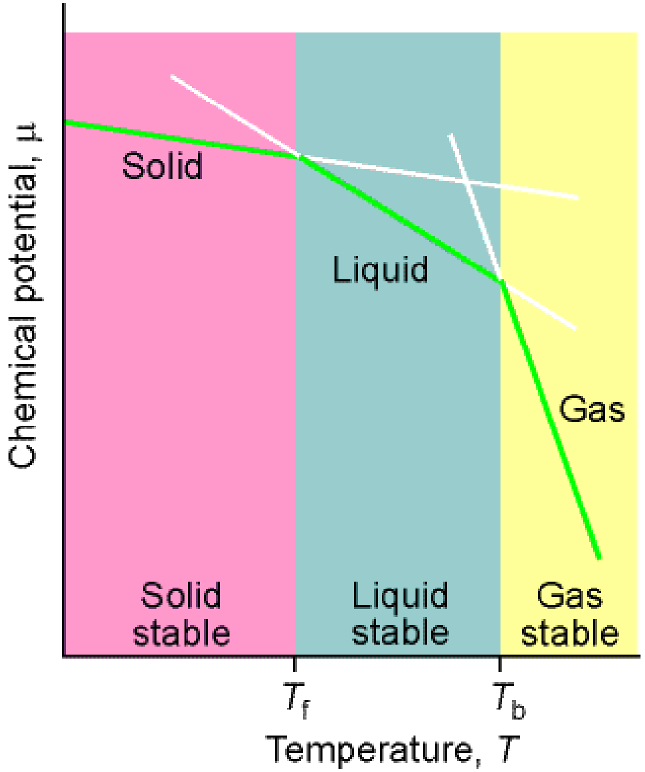
The schematic T dependence of μ of the solid, liquid, and gas phases of a substance

1). The slope of a plot of μ against T is negative.

2). $S_m(g) > S_m(l)$: the slope is steeper for gases than for liquids: and $S_m(l) > S_m(s)$: the slope is steeper for a liquid than the corresponding solid.

6.5 The dependence of stability on the conditions

1) The temperature dependence of phase stability



The schematic T dependence of μ of the solid, liquid, and gas phases of a substance

The steep negative slope of μ (l) results in its falling below μ (s) when T is high enough, and then the liquid becomes the stable phase: the solid melts;

Chemical potential of the gas phase plunges steeply downwards as T is raised; there comes a *temperature* at which it lies lowest. Then the gas is the stable phase and the liquid vaporizes.

6.5 The dependence of stability on the conditions

2) The response of melting to applied pressure

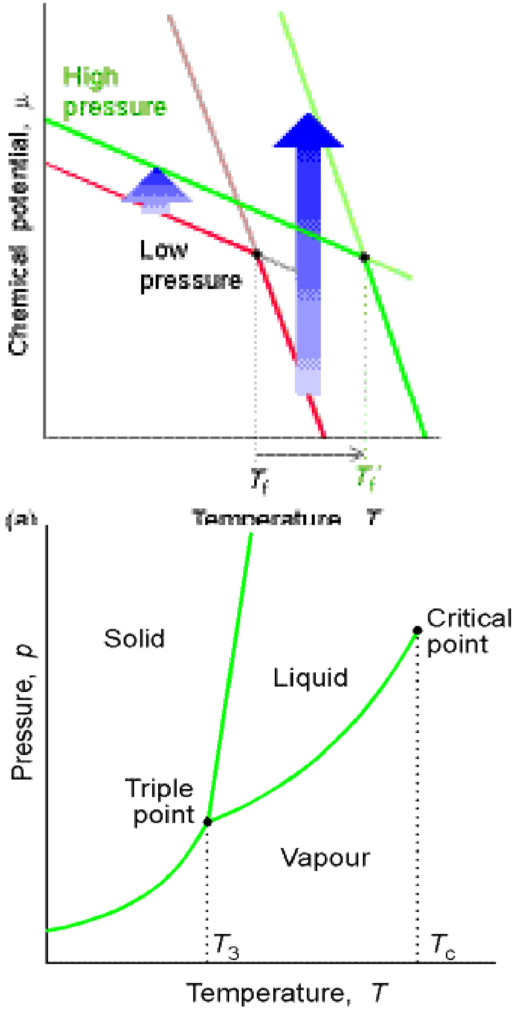
The variation of the chemical potential with pressure is expressed

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_{\mathrm{m}}$$

This equation shows that the slope of a plot of chemical potential against pressure is equal to the molar volume of the substance. An increase in pressure raises the chemical potential of any pure substance (V_{m}>0).

6.5 The dependence of stability on the conditions

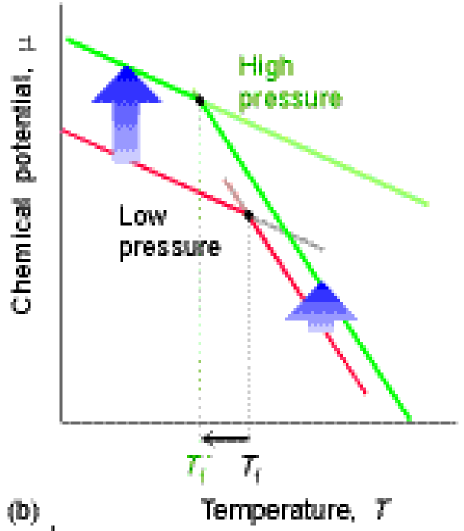
2) The response of melting to applied pressure

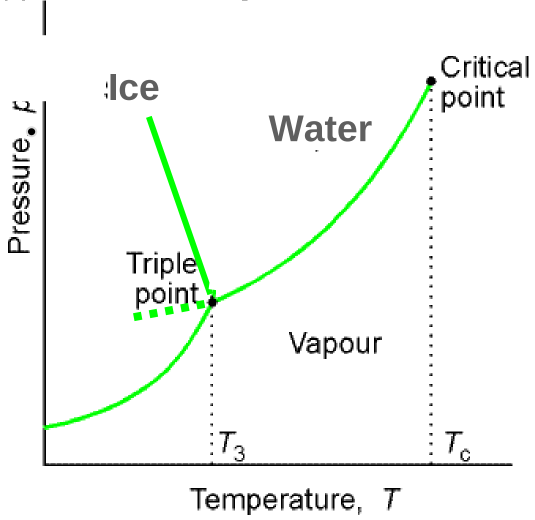


In most cases, $V_m(l) > V_m(s)$ and the above equation predicts that an increase in pressure increases the chemical potential of the liquid more than that of the solid. The effect of pressure in such a case is to raise the melting temperature slightly.

6.5 The dependence of stability on the conditions

2) The response of melting to applied pressure

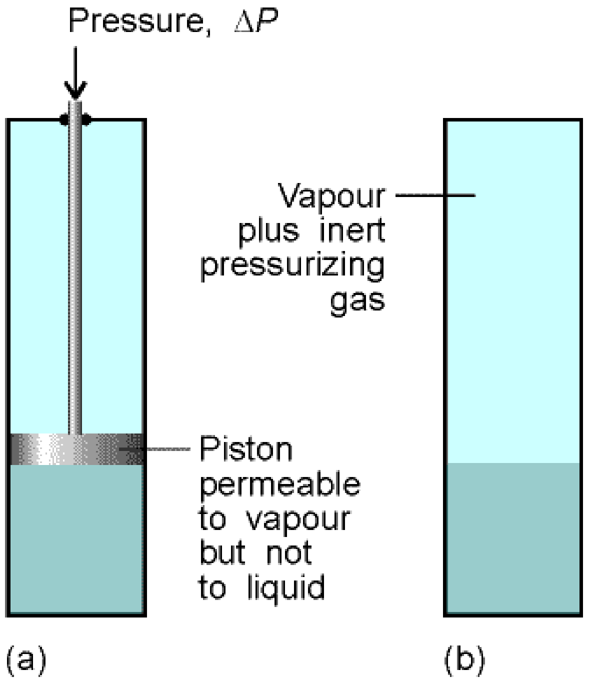




For water, $V_m(s) > V_m(l)$ and an increase in pressure increases the chemical potential of the solid more than that of the liquid. In this case, the melting temperature is lowered slightly.

6.5 The dependence of stability on the conditions

3) The effect of applied pressure on vapour pressure



Pressure applied to a condensed phase 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.

When pressure is applied to a condensed phase, its vapour pressure rises: molecules are squeezed out of the phase and escape as a gas.

6.5 The dependence of stability on the conditions

3) The effect of applied pressure on vapour pressure

The quantitative relation between the vapour pressure, p, when a pressure ΔP is applied and the vapour pressure, p^*, of the liquid in the absence of an additional pressure is derived in the following way.

The calculation of vapour pressure of a pressurized liquid at equilibrium is based on: $\mu(\mathrm{l}) = \mu(\mathrm{g})$

It follows for any change:

$$\mathrm{d}\mu(\mathrm{l}) = \mathrm{d}\mu(\mathrm{g})$$

6.5 The dependence of stability on the conditions

3) The effect of applied pressure on vapour pressure

When the pressure *P* on the liquid is increased by d*P*, the chemical potential of the liquid changes by

$$\mathrm{d}\mu(\mathrm{l}) = V_\mathrm{m}(\mathrm{l})\,\mathrm{d}P$$

and the chemical potential of the vapour changes by

$$\mathrm{d}\mu(\mathrm{g}) = V_\mathrm{m}(\mathrm{g})\,\mathrm{d}p$$

where d*p* is the change in the vapour pressure we are trying to find.

6.5 The dependence of stability on the conditions

3) The effect of applied pressure on vapour pressure

When $V_m(g) = RT/p$, we obtain

$$d\mu(g) = V_m(g)dp = \frac{RT}{p}dp$$

Since $d\mu(l) = d\mu(g)$, and $d\mu(l) = V_m(l)\,dP$, then

$$\frac{RT dp}{p} = V_m(l)dP$$

6.5 The dependence of stability on the conditions

3) The effect of applied pressure on vapour pressure

When there is no additional pressure acting on the liquid, the pressure experienced by the liquid, P, is equal to the normal vapour pressure p^*; so $P = p^*$ and $p = p^*$;

When there is an additional pressure ΔP on the liquid, $P = p + \Delta P$, the vapour pressure is p.

The effect of pressure on the vapour pressure is so small that it is a good approximation to replace the p in $p + \Delta P$ by p^* itself.

6.5 The dependence of stability on the conditions

3) The effect of applied pressure on vapour pressure

$$RT\int_{p^*}^{p}\frac{\mathrm{d}p}{p}=\int_{p^*}^{p^*+\Delta P}V_{\mathrm{m}}(\mathrm{l})\mathrm{d}P$$

Assume that V_{m}(l) of the liquid is the same throughout the small range of pressures involved:

$$RT\ln\frac{p}{p^*}=V_{\mathrm{m}}(\mathrm{l})\Delta P$$

$$p=p^*e^{V_{\mathrm{m}}\Delta P/RT}$$

6.5 The dependence of stability on the conditions

3) The effect of applied pressure on vapour pressure

$$p = p^* e^{V_{\mathrm{m}} \Delta P / RT}$$

This equation shows how the vapour pressure increases when the pressure acting on the condensed phase is increased.

Example

Calculate the effect on the chemical potentials of ice and water of increasing the pressure from 1.00 bar to 2.00 bar at 0℃. The density of ice is 0.917 gcm^{-3} and that of liquid water is 0.999 gcm^{-3} under these conditions.

Example

Method: From equation $\left(\frac{\partial \mu}{\partial p}\right)_T = V_\mathrm{m}$

we know that the change in chemical potential of an incompressible substance when the pressure is changed by Δp is

$$\Delta\mu = V_\mathrm{m}\Delta p$$

To answer the question, we need to know the molar volumes of the two phases of water from the mass density, ρ, and the molar mass, M=18.02 g mol^{-1}

$$V_\mathrm{m} = M/\rho$$

Example

Answer:

$$\Delta\mu(\text{ice}) = \frac{M\Delta p}{\rho}$$

$$= \frac{(1.802\times10^{-2}\,\text{kgmol}^{-1})\times(1.0\times10^{5}\,\text{bar})}{917\text{kgm}^{-3}}$$

$$= 1.97\text{Jmol}^{-1}$$

$$\Delta\mu(\text{water}) = \frac{M\Delta p}{\rho}$$

$$= \frac{(1.802\times10^{-2}\,\text{kgmol}^{-1})\times(1.0\times10^{5}\,\text{bar})}{999\text{kgm}^{-3}}$$

$$= 1.80\,\text{Jmol}^{-1}$$

Example

Estimating the effect of pressure on the vapour pressure

Derive an expression from equation $p = p^{*}e^{V_{\mathrm{m}}\Delta P/RT}$ **that is valid for small changes in vapour pressure and calculate the fractional increase of the vapour pressure of water for an increase in pressure of 10 bar at 25 ℃.**

Example

Method: The question centres on the approximation of the right-hand side of $p = p^* e^{V_\mathrm{m}\Delta P/RT}$ when the exponent is small.

For the approximation, we note that the exponential function e^x is equal to the expansion $1 + x + \frac{1}{2}x^2 + \cdots$;

so if $x \ll 1$, a good approximation is $e^x \approx 1 + x$.

Example

Answer: **If $V_mp/RT \ll 1$, the exponential function on the right of the equation may be approximated by $1+V_mp/RT$:**

$$p = p^* e^{V_m\Delta P/RT}$$

$$= p^*\left(1+\frac{V_m\Delta p}{RT}\right)$$

which rearranges to

$$\frac{p-p^*}{p^*} \approx \frac{V_m\Delta p}{RT}$$

Example

For water (which has density 0.997 g cm^{-3} at 25 ℃ and the molar volume 18.1 cm^{3}mol^{-1})

$$\frac{V_{\mathrm{m}}\Delta p}{RT}=\frac{(1.81\times10^{-5}\,\mathrm{m^{3}mol^{-1}})\times(1.0\times10^{6}\,\mathrm{Pa})}{(8.3145\,\mathrm{JK^{-1}mol^{-1}})\times(298\,\mathrm{K})}=7.3\times10^{-3}$$

Since $\frac{V_{\mathrm{m}}\Delta p}{RT}<<1$ **the formula can be used**

$\frac{p-p^{*}}{p^{*}}=7.3\times10^{-3}$, **an increase of 0.73 per cent.**

6. Physical transformation of pure substances

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6.6 The location of phase boundaries ▶

6.7 The Ehrenfest classification of phase transitions

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6.8 Surface tension

6.9 Curved surfaces

6.10 Capillary action

6.6 The location of phase boundaries

The thermodynamic criterion of equilibrium:

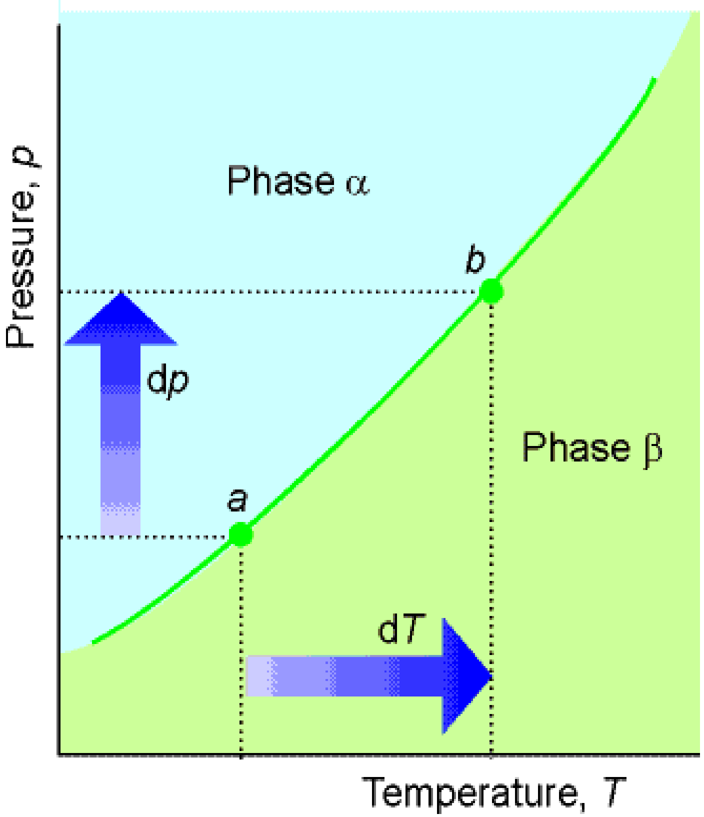
At equilibrium, the chemical potential of a substance is the same throughout a sample, regardless of how many phases are present.

Where the phases α and β are in equilibrium

$$\mu_\alpha(p,T) = \mu_\beta(p,T)$$

6.6 The location of phase boundaries

1) The slopes of the phase boundaries



$$d\mu_\alpha = d\mu_\beta$$

$$dG = -SdT + Vdp$$

$$d\mu = dG_m = -S_m dT + V_m dp$$

For each phase, it follows that

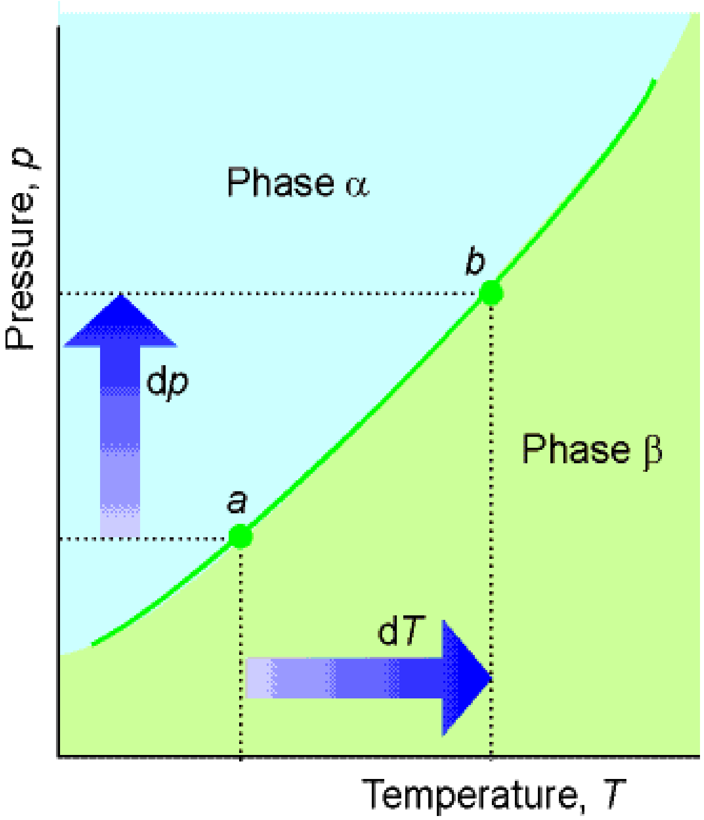
$$-S_{\alpha,m}dT + V_{\alpha,m}dp = -S_{\beta,m}dT + V_{\beta,m}dp$$

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

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

6.6 The location of phase boundaries

1) The slopes of the phase boundaries



The Clapeyron equation

$$\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{\Delta_{\mathrm{trs}}S}{\Delta_{\mathrm{trs}}V}$$

The Clapeyron equation is an exact expression for the slope of the phase boundary and applies to any phase equilibrium of any pure substance.

6.6 The location of phase boundaries

2) The solid-liquid boundary

Melting (fusion) is accompanied by a molar enthalpy change $\Delta_{\text{fus}}H$ and a molar volume change $\Delta_{\text{fus}}V$ occurs at a temperature T, and $\Delta_{\text{fus}}S = \Delta_{\text{fus}}H / T$.

The Clapeyron equation becomes

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\text{fus}}H}{T\Delta_{\text{fus}}V}$$

The enthalpy of melting is positive and the volume change is usually positive and always small. Consequently, the slope $\mathrm{d}p/\mathrm{d}T$ is steep and usually positive.

6.6 The location of phase boundaries

2) The solid-liquid boundary

Assuming that $\Delta_{\text{fus}}H$ and $\Delta_{\text{fus}}V$ change so little with temperature and pressure that they can be treated as constant. If the melting temperature is T^* when the pressure is p^*, and T when the pressure is p , the integration is

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\text{fus}}H}{T\Delta_{\text{fus}}V} \qquad \int_{p^*}^{p}\mathrm{d}p == \frac{\Delta_{\text{fus}}H}{\Delta_{\text{fus}}V}\int_{T^*}^{T}\frac{\mathrm{d}T}{T}$$

Therefore, the approximate equation of the solid-liquid boundary is

$$p = p^* + \frac{\Delta_{\text{fus}}H}{\Delta_{\text{fus}}V}\ln\frac{T}{T^*}$$

6.6 The location of phase boundaries

2) The solid-liquid boundary

When T is close to T^*, by approximation

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

because $\ln(l+x)\approx 1$ when $x \ll 1$; therefore

$$p=p^*+\frac{\Delta_{\text{fus}}H}{\Delta_{\text{fus}}V}\ln\frac{T}{T^*}$$

$$p\approx p^*+\frac{(T-T^*)\Delta_{\text{fus}}H}{T^*\Delta_{\text{fus}}V}$$

6.6 The location of phase boundaries

3) The liquid-vapour boundary

The entropy of vaporization at a temperature *T* is equal

$$\Delta_{\mathrm{vap}}S = \Delta_{\mathrm{vap}}H/T$$

The Clapeyron equation for the liquid-vapour boundary

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}S}{\Delta_{\mathrm{vap}}V} \Rightarrow \frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}H}{T\Delta_{\mathrm{vap}}V}$$

6.6 The location of phase boundaries

3) The liquid-vapour boundary

Since $V_m(g) >> V_m(l)$, then

$$\Delta_{vap}V = (V_m(g) - V_m(l)) \approx V_m(g)$$

And if the gas behaves perfectly, $V_m(g) = RT/p$

The Clapeyron equation is changed into

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T(RT/p)} \quad \Rightarrow \quad \frac{dp}{p}\frac{1}{dT} = \frac{\Delta_{vap}H}{RT^2}$$

$$\frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}$$

6.6 The location of phase boundaries

3) The liquid-vapour boundary

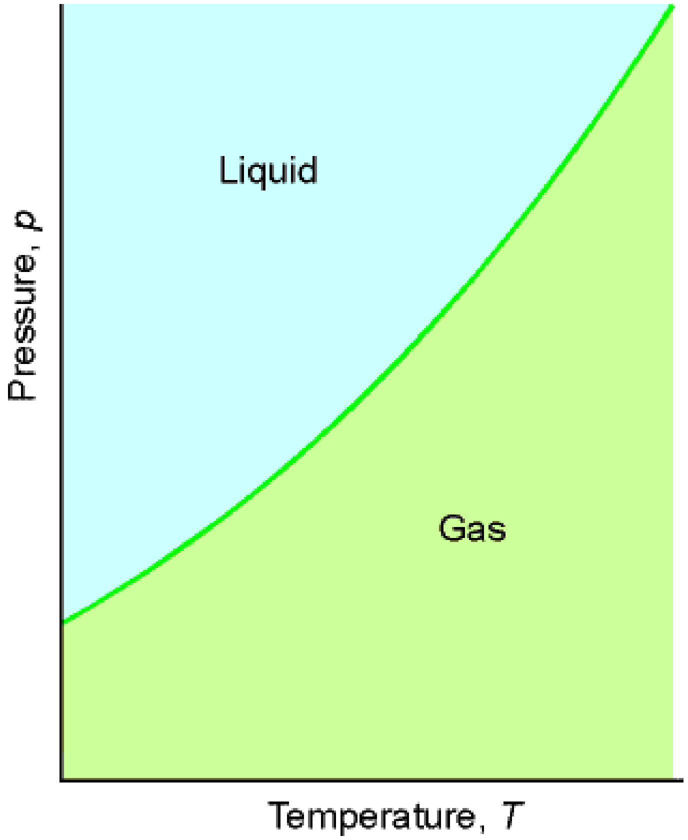
If we also assume that the enthalpy of vaporization is independent of *T*, the above equation integrates to

$$p = p^{*} e^{-\chi} \qquad \chi = \frac{\Delta_{\text{vap}} H}{R}\left(\frac{1}{T} - \frac{1}{T^{*}}\right)$$

Where *p is the vapour pressure when the temperature is *T** and *p* the vapour pressure when the temperature is *T*.**

6.6 The location of phase boundaries

3) The liquid-vapour boundary



$$p = p^* e^{-\chi} \qquad \chi = \frac{\Delta_{\mathrm{vap}} H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

The above equations are the curve plotted as the liquid-vapour boundary. The line does not extend beyond T_c, because above this T_c the liquid does not exist.

Example

Estimating the effect of pressure on the boiling point

Estimate the typical size of the effect of increasing pressure on the boiling point of a liquid.

Example

Method: $$\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{\Delta_{\mathrm{vap}}H}{T\Delta_{\mathrm{vap}}V}$$

To use this equation, we need to estimate the right-hand side. At the boiling point, the term $\Delta_{\mathrm{vap}}H\,/T$ is Trouton's constant (Section 4.3a). Because the molar volume of a gas is so much greater than the molar volume of a liquid, then

$$\Delta_{\mathrm{vap}}V=(V_{\mathrm{m}}(\mathrm{g})-V_{\mathrm{m}}(\mathrm{l}))\approx V_{\mathrm{m}}(\mathrm{g})$$

Example

Answer: Trouton's constant has the value 85 $JK^{-1}mol^{-1}$. The molar volume of a perfect gas is about 25 L mol^{-1} at 1 atm and near but above T_{room}.

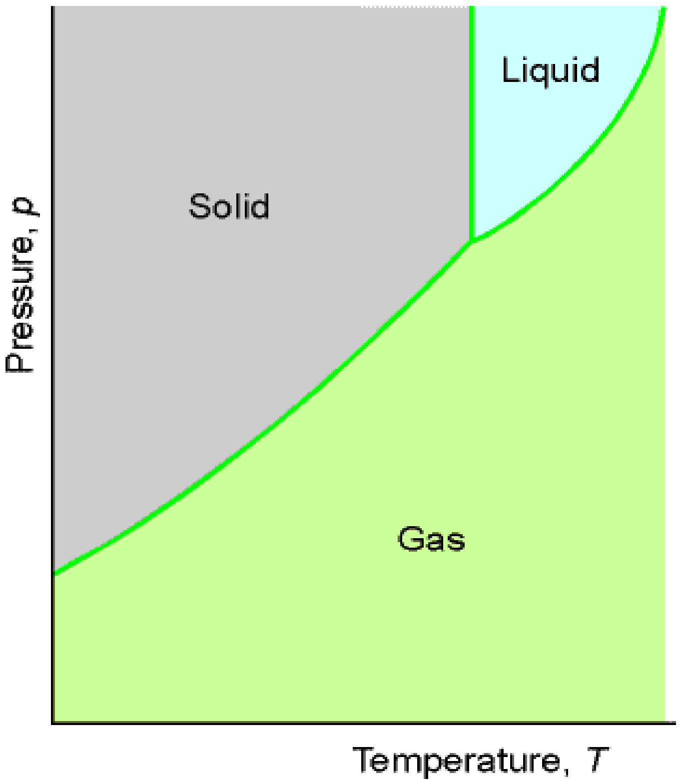
$$\frac{dp}{dT} \approx \frac{\Delta_{vap}H}{T\Delta_{vap}V} = \frac{85 JK^{-1} mol^{-1}}{25\times10^{-3} m^3 nol^{-1}} = 3.4\times10^3 PaK^{-1}$$

This value corresponds to 0.034 atm K^{-1}, and hence to dT/dp = 30 atm K^{-1}. Therefore, a change of p of + 0.1 atm can be expected to change a T_b by about +3K.

6.6 The location of phase boundaries

4) The solid-vapour boundary

$$p = p^* e^{-\chi} \qquad \chi = \frac{\Delta_{\text{sub}}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$



Because the enthalpy of sublimation is greater than the enthalpy of vaporization, the equation predicts a steeper slope for the sublimation curve than for the vaporization curve at similar temperatures, which is near where they meet

Summary on Sec. 6.6

1) The slopes of the phase boundaries

The Clapeyron equation $\dfrac{\mathrm{d}p}{\mathrm{d}T}=\dfrac{\Delta_{\mathrm{trs}}S}{\Delta_{\mathrm{trs}}V}$

2) S-L $\dfrac{\mathrm{d}p}{\mathrm{d}T}=\dfrac{\Delta_{\mathrm{fus}}H}{T\Delta_{\mathrm{fus}}V}$ $\quad p\approx p^{*}+\dfrac{(T-T^{*})\Delta_{\mathrm{fus}}H}{T^{*}\Delta_{\mathrm{fus}}V}$

3) L-V $\dfrac{\mathrm{d}p}{\mathrm{d}T}=\dfrac{\Delta_{\mathrm{vap}}H}{T\Delta_{\mathrm{vap}}V}$ $\quad p=p^{*}e^{-\chi}$ $\quad \chi=\dfrac{\Delta_{\mathrm{vap}}H}{R}\left(\dfrac{1}{T}-\dfrac{1}{T^{*}}\right)$

4) S-V $\dfrac{\mathrm{d}p}{\mathrm{d}T}=\dfrac{\Delta_{\mathrm{sub}}H}{T\Delta_{\mathrm{sub}}V}$ $\quad p=p^{*}e^{-\chi}$ $\quad \chi=\dfrac{\Delta_{\mathrm{sub}}H}{R}\left(\dfrac{1}{T}-\dfrac{1}{T^{*}}\right)$

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▶

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6.7 The Ehrenfest classification of phase transitions

1) The first-order phase transition

There are many different types of phase transition, and thermodynamic properties of substances may be used to classify phase transitions into different types.

At equilibrium, $\mu(\alpha) = \mu(\beta)$, $\Delta G = 0$,

but, $\Delta H \neq 0$, $\Delta S \neq 0$, $\Delta V \neq 0$.

These changes have implications for the slopes of the chemical potentials of the phases at either side of the phase transition.

6.7 The Ehrenfest classification of phase transitions

1) The first-order phase transition

At the transition from a phase a to another phase

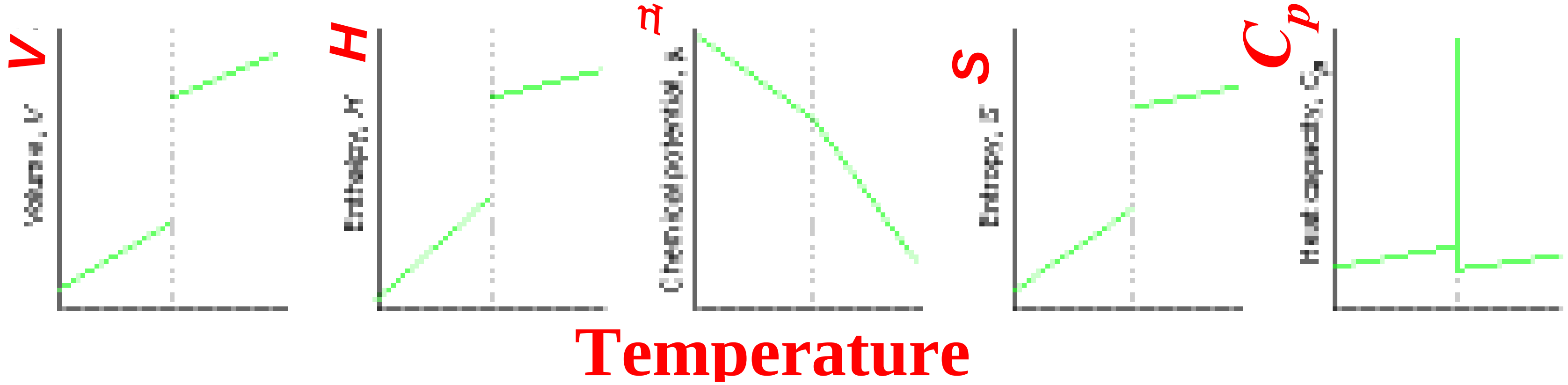
$$\left(\frac{\partial \mu_\beta}{\partial p}\right)_T - \left(\frac{\partial \mu_\alpha}{\partial p}\right)_T = V_{\beta,\mathrm{m}} - V_{\beta,\mathrm{m}} = \Delta_{\mathrm{trs}} V$$

$$\left(\frac{\partial \mu_\beta}{\partial T}\right)_p - \left(\frac{\partial \mu_\alpha}{\partial T}\right)_p = S_{\beta,\mathrm{m}} - S_{\beta,\mathrm{m}} = -\Delta_{\mathrm{trs}} S = \frac{\Delta_{\mathrm{trs}} H}{T_{\mathrm{trs}}}$$

Because $\Delta_{\mathrm{trs}}H \neq 0$ and $\Delta_{\mathrm{trs}}V \neq 0$ for melting and vaporization, it follows that for such transitions the slopes of the chemical potential plotted against either pressure or temperature are different on either side of the transition.

6.7 The Ehrenfest classification of phase transitions

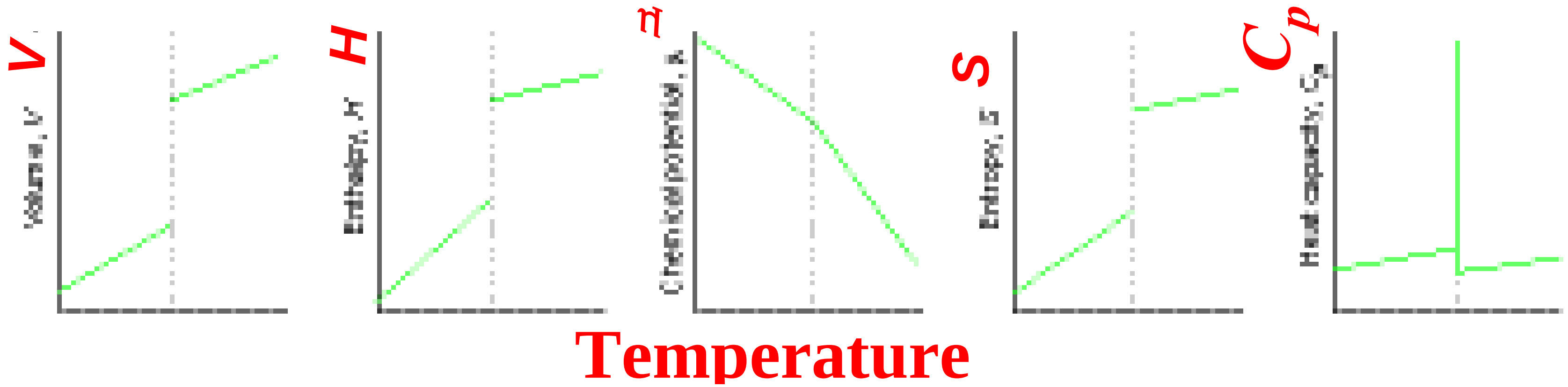
1) The first-order phase transition



A transition for which the first derivative of chemical potentials with respect to temperature is discontinuous is classified as a first-order phase transition.

6.7 The Ehrenfest classification of phase transitions

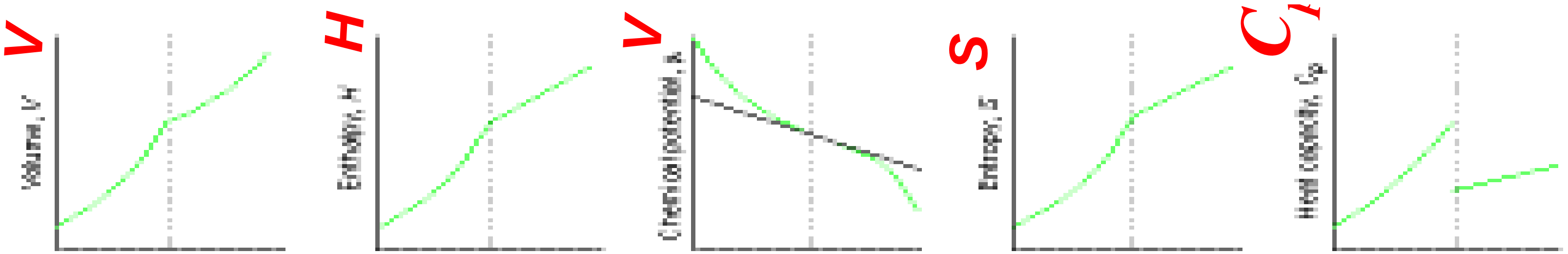
1) The first-order phase transition



The constant pressure heat capacity C_p of a substance is the slope of a plot of the enthalpy with respect to T. At a first-order phase transition, H changes by a finite amount for an infinitesimal change of temperature. Therefore, C_p is infinite at the transition.

6.7 The Ehrenfest classification of phase transitions

2) The second-order phase transition

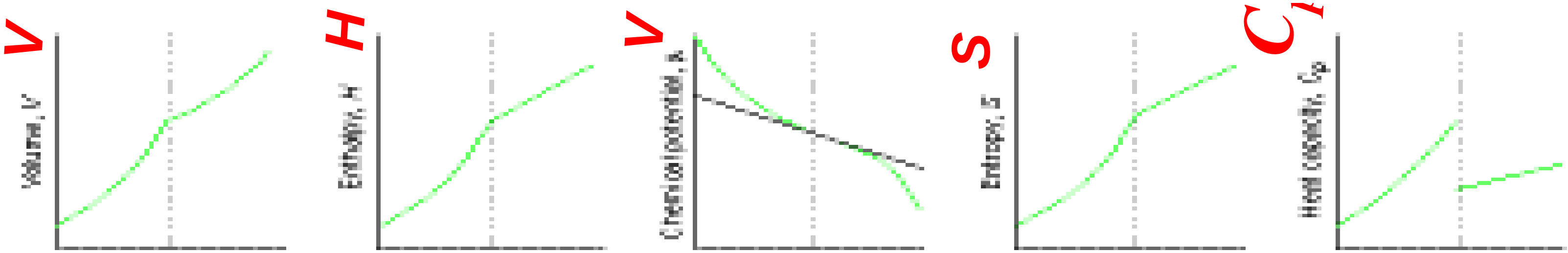


Temperature

A phase transition for which the first derivative of μ with respect to temperature is continuous but its second derivative is discontinuous is called the second-order phase transition.

6.7 The Ehrenfest classification of phase transitions

2) The second-order phase transition



Temperature

A continuous slope of μ implies that the V and S (and H) do not change at the transition. The C_p is discontinuous at the transition but does not become infinite there.

6.7 The Ehrenfest classification of phase transitions

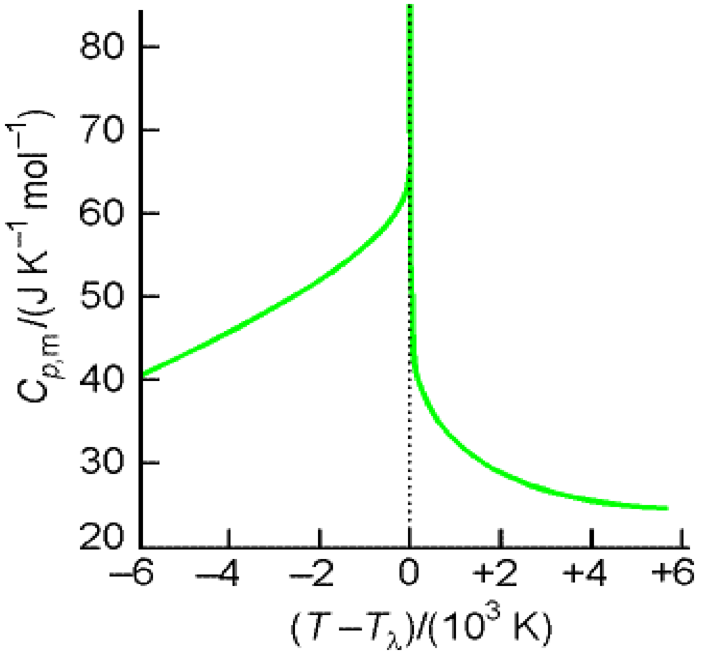
3) λ− transition.

The term λ−transition is applied to a phase transition that is not first-order yet the heat capacity becomes infinite at the transition temperature.

Typically, the heat capacity of a system that shows such a transition begins to increase well before the transition and the shape of the heat capacity curve resembles the Greek letter lambda.

6.7 The Ehrenfest classification of phase transitions

3) λ− transition.



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.

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6.8 Surface tension ▶

6.9 Curved surfaces

6.10 Capillary action

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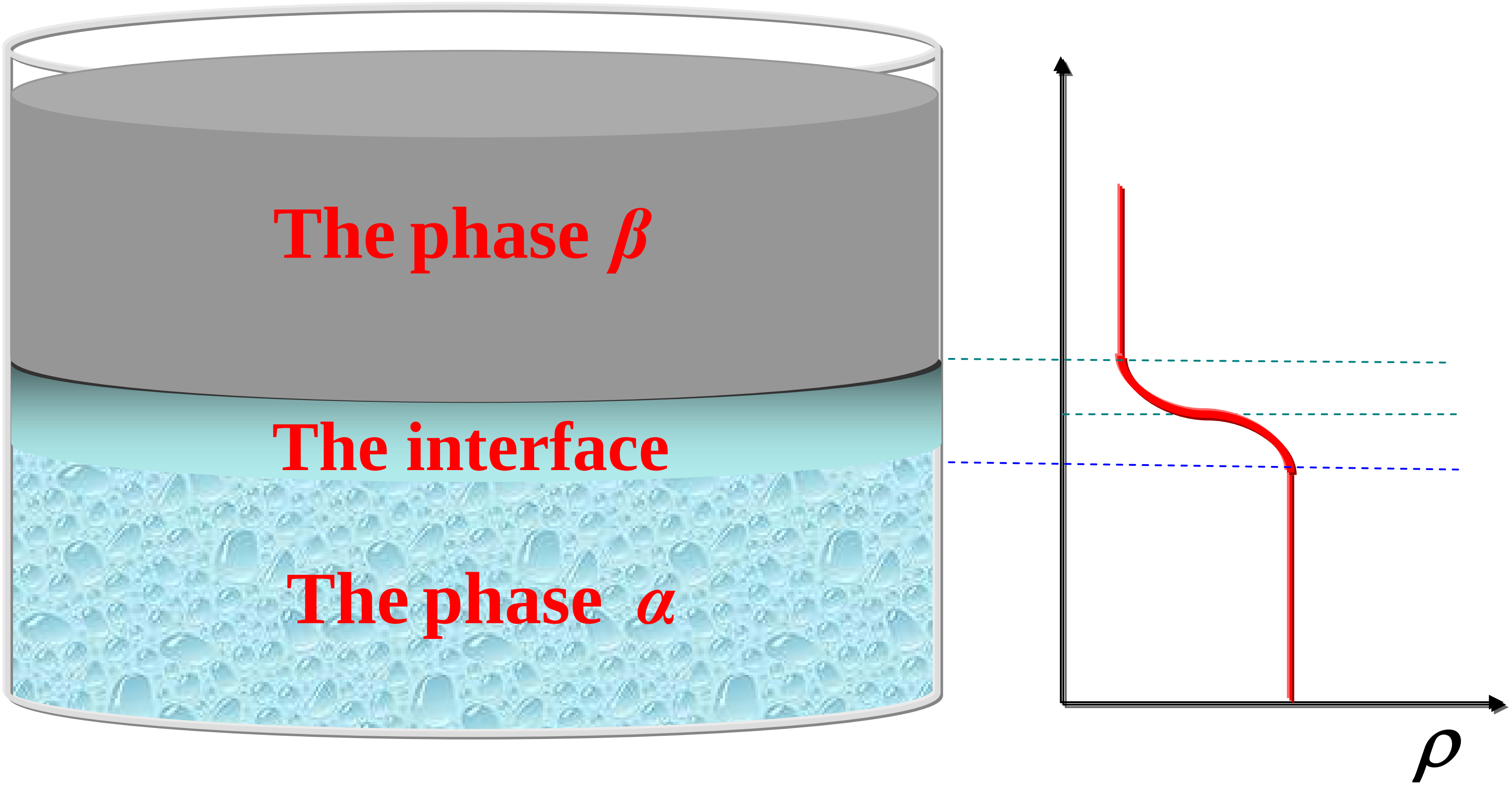
The physical liquid surface

We have concentrated on the properties of the boundaries in the phase diagram of a substance. However, the physical boundary between phases, such as the surface where solid is in contact with liquid or liquid is in contact with vapour, has interesting properties. In this section we concentrate on the liquid-vapour interface, which is interesting because it is so mobile. Chapter 28 deals with solid surfaces and their important role in catalysis.

The physical liquid surface

0. Interfaces



The physical liquid surface

0. Types of interfaces

L/G –The liquid/gas interface

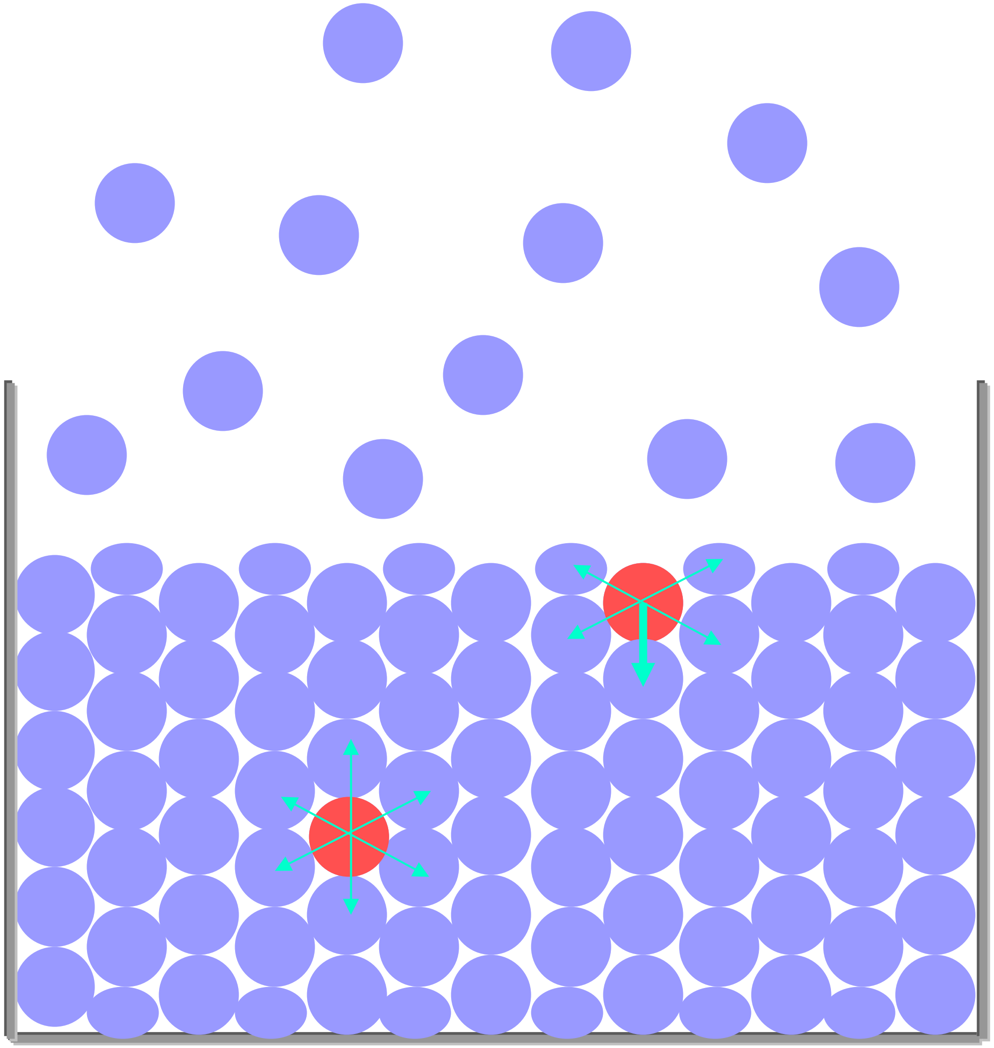
L/L –The liquid/liquid interface

L/S – The liquid/solid interface

S/S – The solid/solid interface

S/G – The solid/gas interface

The physical liquid surface



The physical liquid surface

Liquids tend to adopt shapes that minimize their surface area, for then the maximum number of molecules are in the bulk and hence surrounded by and interacting with neighbors. Droplets of liquids therefore tend to be spherical, because a sphere is the shape with the smallest surface-to-volume ratio.

The physical liquid surface

The surface tension

Surface effects may be expressed in terms of Helmholtz and Gibbs energies. and that dA and dG are equal to the work done in changing the energy of a system.The work needed to change the surface area, σ, of a sample by an infinitesimal amount dσ is proportional to dσ:

$$dw = \gamma \mathrm{d}\sigma$$

The physical liquid surface

The surface tension

$$dw = \gamma \mathrm{d}\sigma$$

The constant of proportionality, γ, is called the surface tension; its dimensions are energy/area and its units are typically Jm^{-2}. The values of γ are usually reported in Nm^{-1} (1 J = 1 Nm).

The physical liquid surface

The work of surface formation at constant V and T can be identified with the change in the Helmholtz energy:

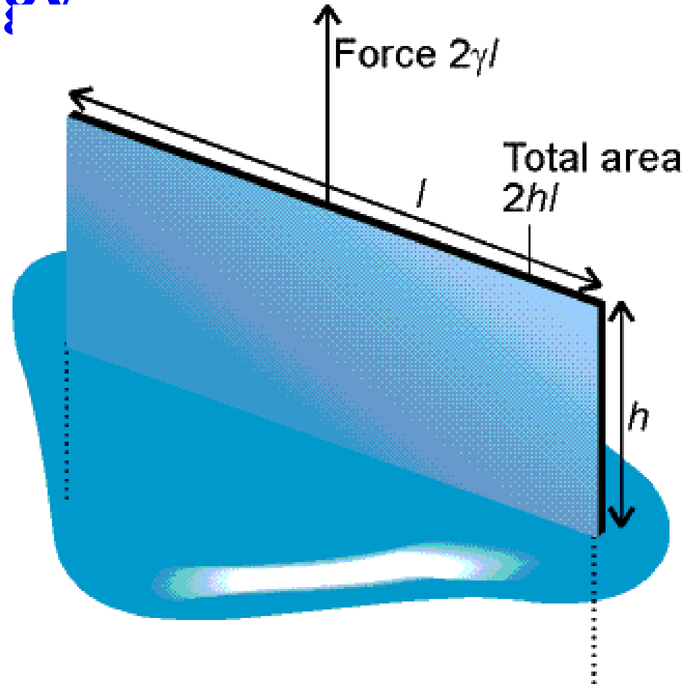
$$dA = \gamma \mathrm{d}\sigma$$

Because dA <0 if d σ <0, surfaces have a natural tendency to contract. This is a more formal way of expressing what we have already described

Example

Using the surface tension

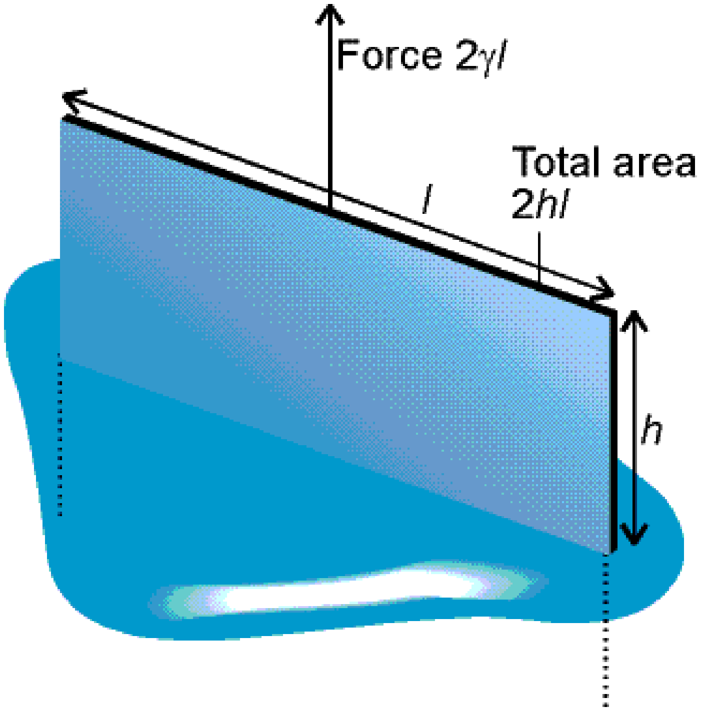
Calculate the work needed to raise a wire of length *l* and to stretch the surface of a liquid through a eight *h* in the arrangement. Disregard gravitational potential energy



Example

Method: The work required to create a surface area given that the surface tension does not vary as the surface is formed is $w = \gamma\sigma$. So, all we need do is to calculate the surface area of the **two-sided** rectangle formed as the frame is withdrawn from the liquid.

Example



Answer: When the wire of length *l* is raised through a height *h* it increases the area of the liquid by twice the area of the rectangle.

The total increase of the area $\sigma = 2hl$:

The work done is $W = \gamma\sigma = 2\gamma lh$.

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0. Bubbles, cavities, and droplets

A bubble: a region in which vapour is trapped by a thin film;

A cavity: a vapour-filled hole in a liquid. What are widely called 'bubbles' in liquids are therefore strictly cavities. True bubbles have two surfaces (one on each side of the film); cavities have only one. The T of both are similar, but a factor of 2 is required for bubbles to take into account the doubled surface area.

A droplet: a small volume of liquid at equilibrium surrounded by its vapour.

6.9 Curved surfaces

1) Laplace equation

The cavities in a liquid are at equilibrium when the tendency for their surface area to decrease is balanced by the rise of internal pressure that would then result.

When the pressure inside a cavity is p_{in} and its radius is r, the outward force is $F_1 = 4\pi r^2 p_{in}$

The force inwards F_2 arises from the external pressure $F_e = 4\pi r^2 p_{out}$ and the surface tension F_γ. F_γ is as follows

6.9 Curved surfaces

1) Laplace equation

The change in surface area when the radius of a sphere changes from r to r + dr is:

$$\mathrm{d}\sigma = 4\pi(r + \mathrm{d}r)^2 - 4\pi r^2 = 8\pi r\,\mathrm{d}r \quad (\mathrm{d}r^2 \text{ is ignored})$$

The work done when the surface is stretched by this amount is: $\mathrm{d}w = 8\gamma\pi r\mathrm{d}r$

The force opposing stretching through a distance dr when the radius is r is : $F_\gamma = 8\gamma\pi r$

The total inward force $F_2 = F_e + F_\gamma$

At equilibrium, the outward and inward forces are balanced: $F_1 = F_2$

6.9 Curved surfaces

1) Laplace equation

$$F_1 = F_2 = F_e + F_\gamma$$

$$F_1 = 4\pi r^2 p_{in} \qquad F_e = 4\pi r^2 p_{out} \qquad F_\gamma = 8\gamma\pi r$$

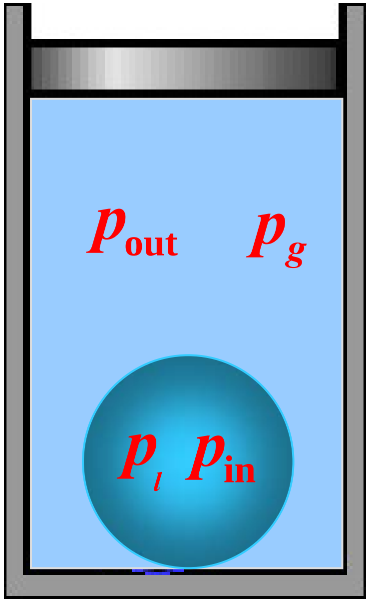
$$4\pi r^2 p_{in} = 4\pi r^2 p_{out} + 8\gamma\pi r$$

$$p_{in} = p_{out} + \frac{2\gamma}{r}$$ **Laplace equation**

The pressure on the concave side of an interface, p_{in}, is always greater than that on the convex side, p_{out}. This relation is expressed by the Laplace equation.

6.9 Curved surfaces

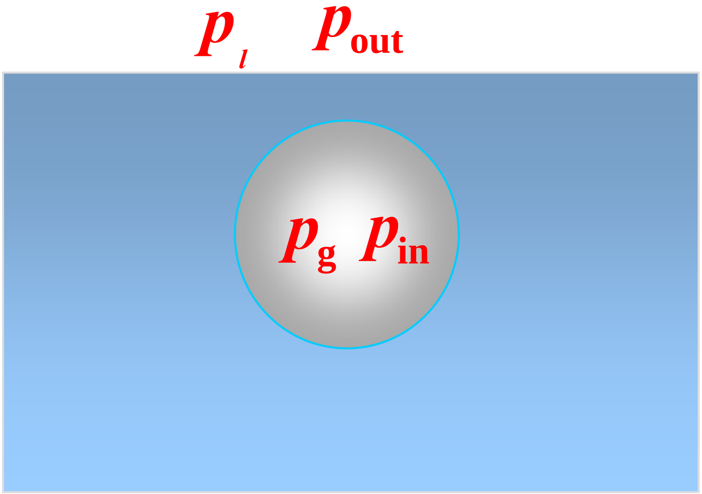
droplet



$$p_{\text{in}} = p_{\text{out}} + \frac{2\gamma}{r}$$

$$p_l = p_g + \frac{2\gamma}{r}$$

bubble



$$p_{\text{in}} = p_{\text{out}} + \frac{2\gamma}{r}$$

$$p_l = p_g - \frac{2\gamma}{r}$$

6.9 Curved surfaces

2) Kelvin equation

The vapour pressure of a liquid depends on the pressure applied to the liquid as the following equation

$$p = p^* e^{V_{\mathrm{m}} \Delta P / RT}$$

Because curving a surface gives rise to a pressure differential of $2\gamma/r$, the vapour pressure above a curved surface may be different from that above a flat surface. By substituting this value of the pressure difference into the above equation we obtain the **Kelvin equation**.

6.9 Curved surfaces

2) Kelvin equation

For the vapour pressure of a liquid when it is dispersed as droplets of radius *r*:

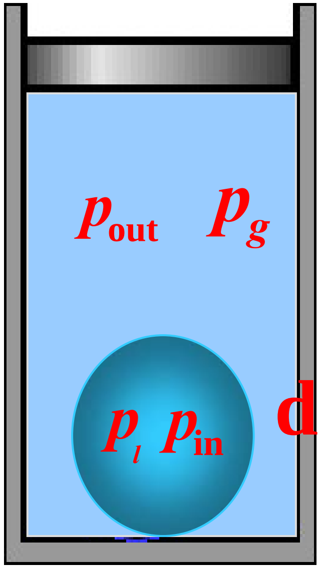
$$p_l = p_{\mathrm{g}} + \frac{2\gamma}{r} \Rightarrow \Delta p = \frac{2\gamma}{r} \Rightarrow p = p^* e^{2\gamma V_{\mathrm{m}}/rRT}$$

The pressure of the liquid outside the cavity is less than the pressure inside, so for the vapour pressure inside a cavity :

$$p_l = p_{\mathrm{g}} - \frac{2\gamma}{r} \Rightarrow \Delta p = -\frac{2\gamma}{r} \Rightarrow p = p^* e^{-2\gamma V_{\mathrm{m}}/rRT}$$

Summary

Laplace equation | **Kelvin equation**

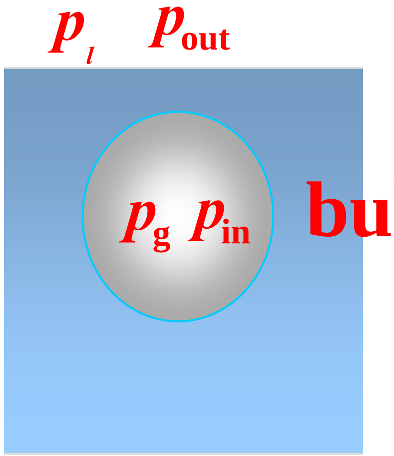


droplet

$$p_{in} = p_{out} + \frac{2\gamma}{r}$$

$$p_l = p_g + \frac{2\gamma}{r}$$

$$p = p^* e^{\left(\frac{2\gamma V_m}{rRT}\right)}$$



bubble

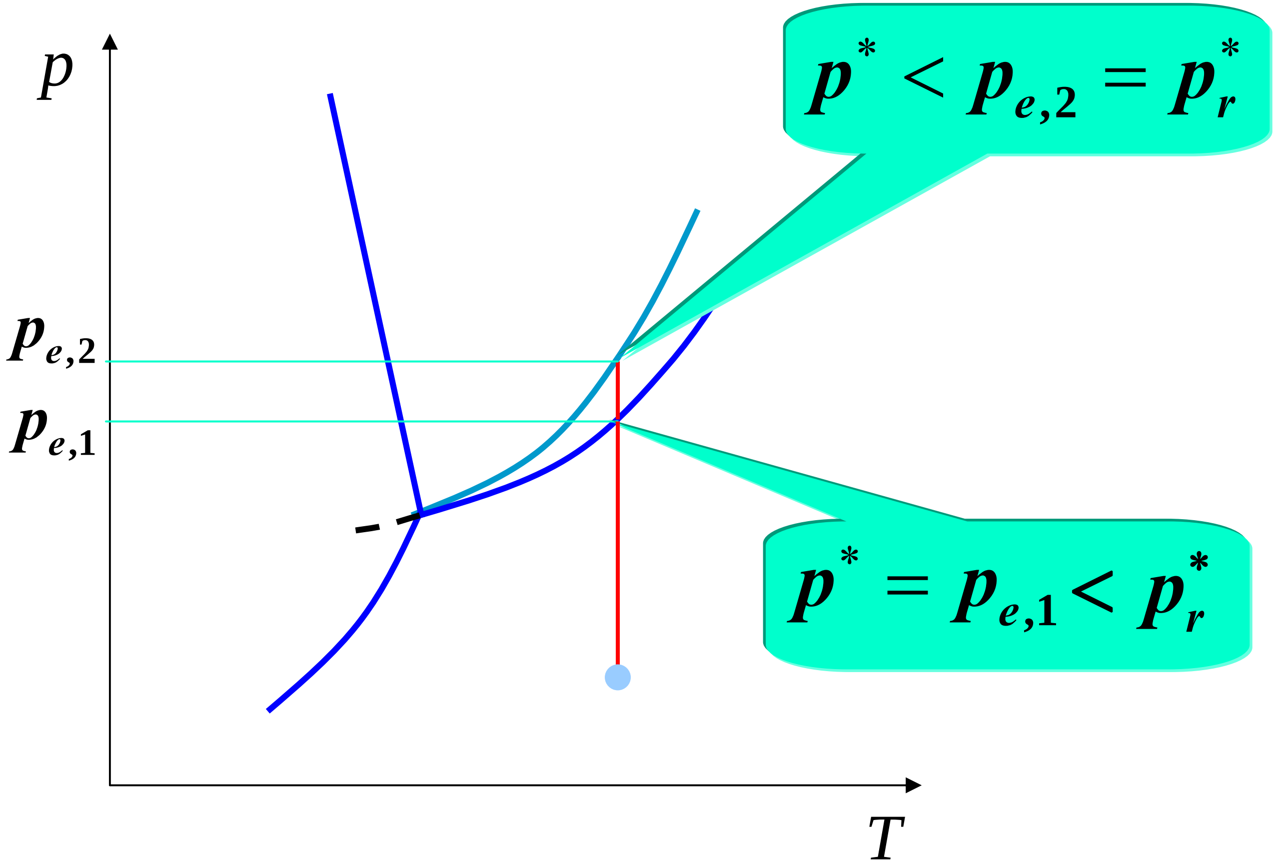
$$p_{in} = p_{out} + \frac{2\gamma}{r}$$

$$p_l = p_g - \frac{2\gamma}{r}$$

$$p = p^* e^{-\left(\frac{2\gamma V_m}{rRT}\right)}$$

6.9 Curved surfaces −3) Nucleation

3.1) The supersaturated vapour



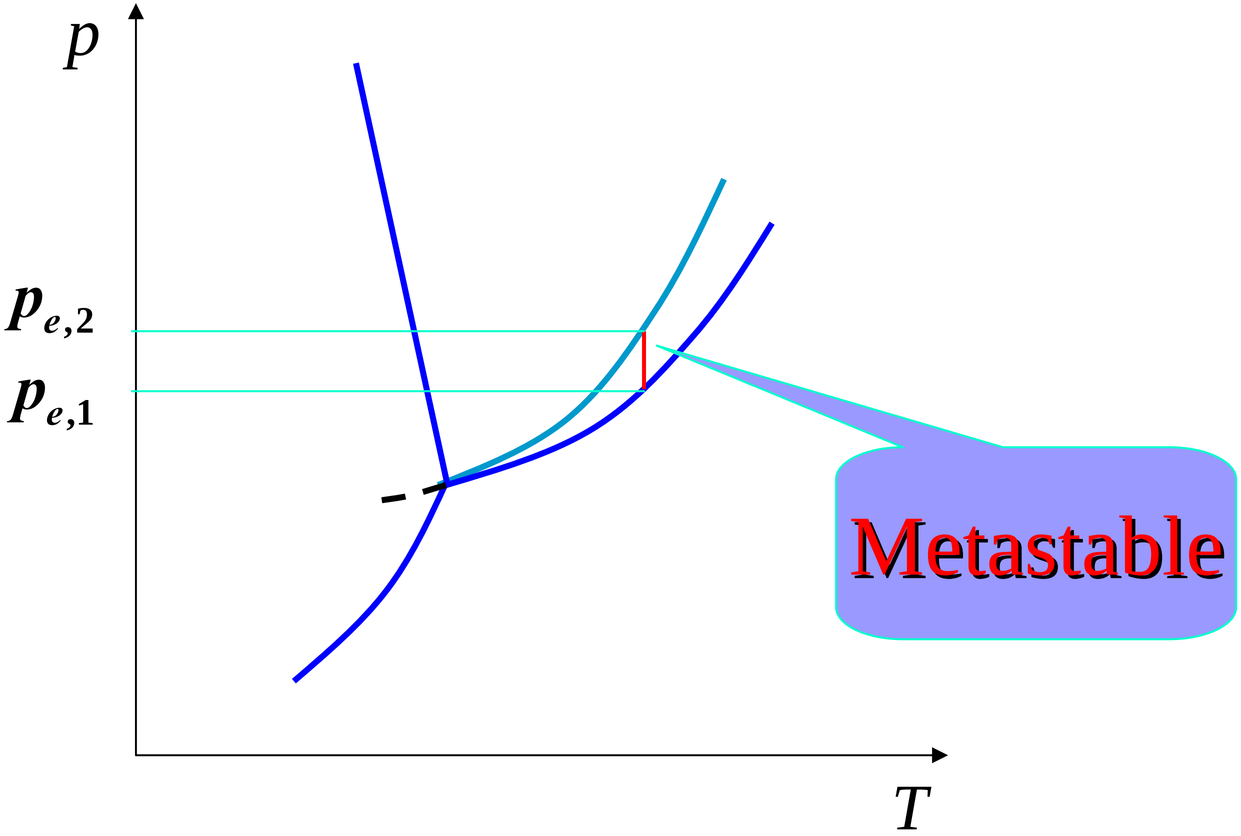
$p^* < p_{e,2} = p_r^*$

$p^* = p_{e,1} < p_r^*$

▨ **Nucleate−dust and particle**

6.9 Curved surfaces

3.1) The supersaturated vapour

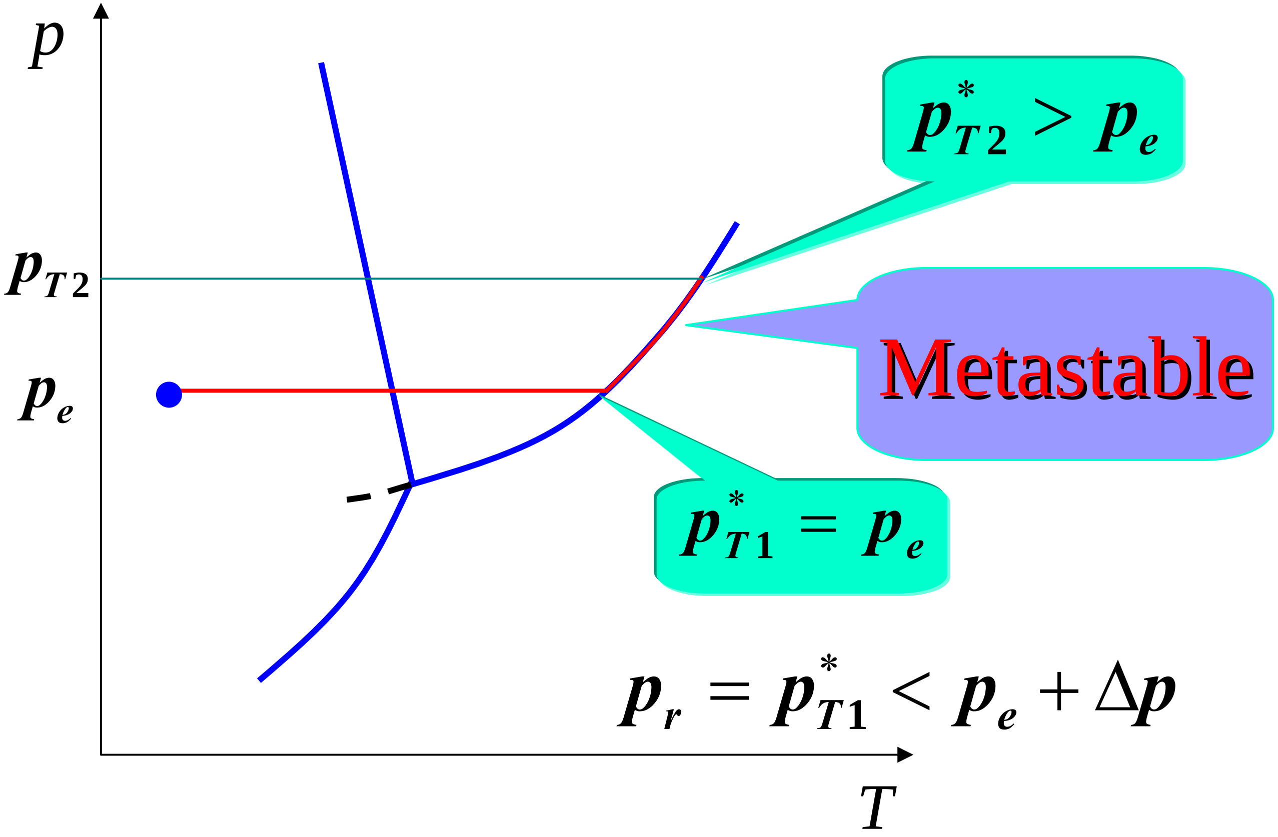


Metastable

6.9 Curved surfaces

3.2) The superheated liquid

$$p_r = p_{T2}^* = p_e + \Delta p$$



$p_{T2}^* > p_e$

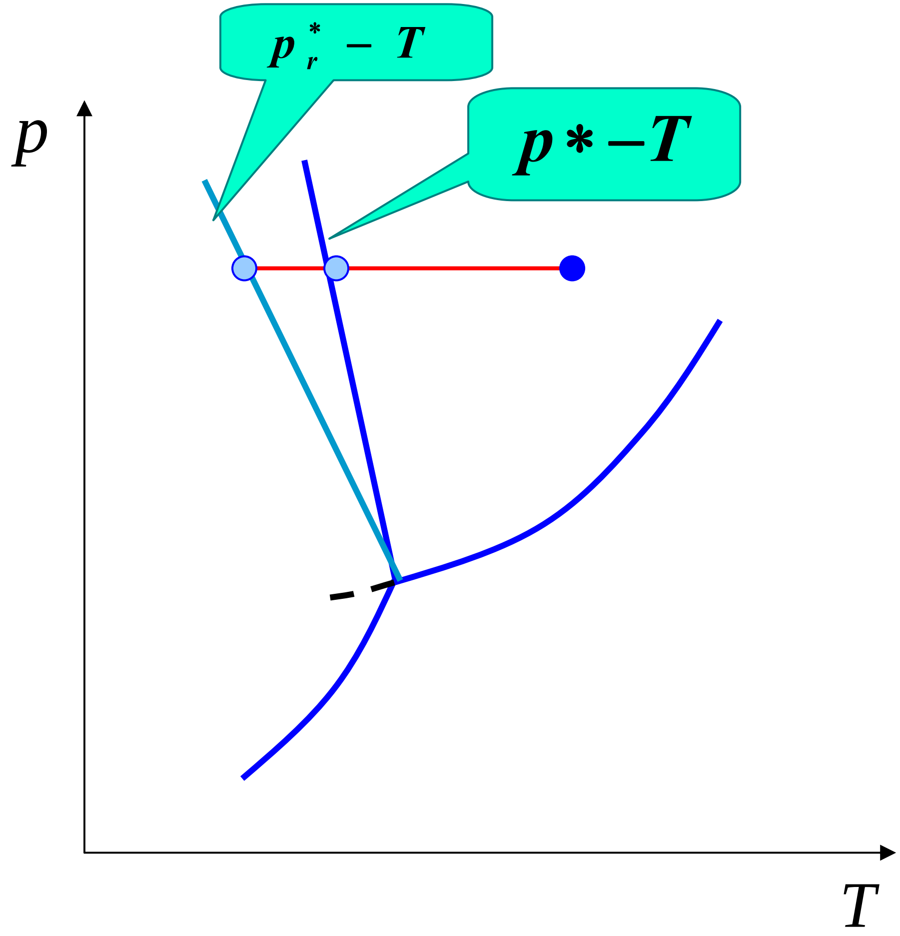
$p_{T1}^* = p_e$

$$p_r = p_{T1}^* < p_e + \Delta p$$

- Nucleate-small pieces of sharp-edged glass

6.9 Curved surfaces

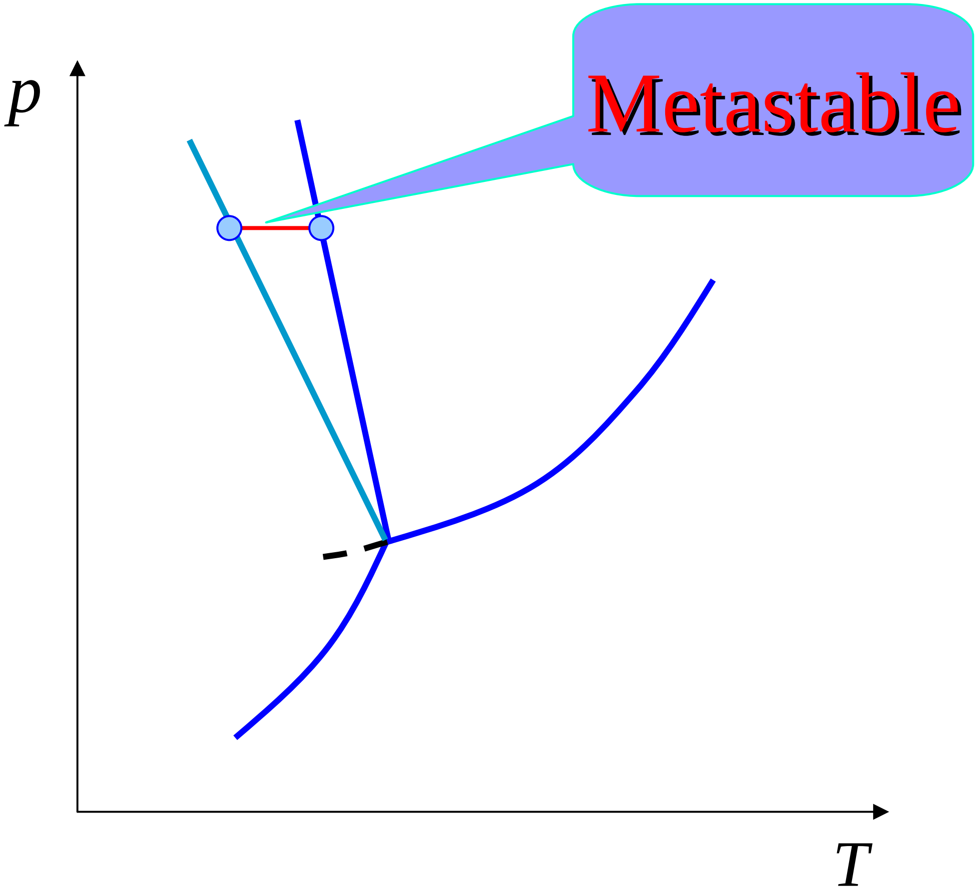
3.3) The supercooled liquid



- **Nucleate**

6.9 Curved surfaces

3.1) The superheated liquid



6. Physical transformation of pure substances

Phase diagrams

6.1 The stabilities of phases

6.2 Phase boundaries

6.3 Three typical phase diagrams

Phase stability and phase transitions

6.4 The thermodynamic criterion of equilibrium

6.5 The dependence of stability on the conditions

6.6 The location of phase boundaries

6.7 The Ehrenfest classification of phase transitions

The physical liquid surface

6.8 Surface tension

6.9 Curved surfaces

6.10 Capillary action ▶

6.10 Capillary action

$$p_2^{(l)} = p_1^{(l)} + \rho^{(l)} gh$$

$$p_2^{(g)} = p_1^{(g)} + \rho^{(g)} gh$$

$$p_1^{(l)} + \rho^{(l)} gh = p_1^{(g)} + \rho^{(g)} gh$$

$$p_1^{(l)} = p_1^{(g)} - (\rho^{(l)} - \rho^{(g)}) gh$$

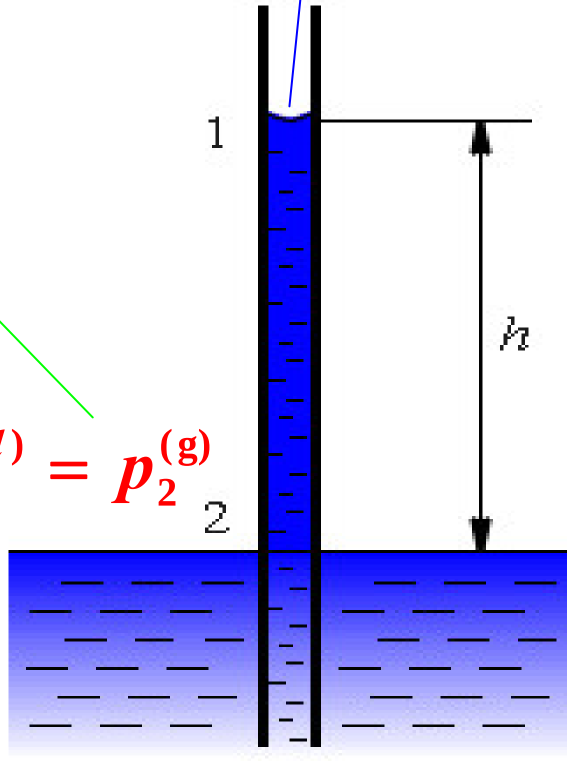
$$\frac{2\gamma}{r} = \left(\rho^{(l)} - \rho^{(g)}\right) gh$$

$$\rho^{(l)} >> \rho^{(g)}$$

$$h = \frac{2\gamma}{rg\rho^{(l)}} \qquad \gamma = \frac{hrg\rho^{(l)}}{2}$$

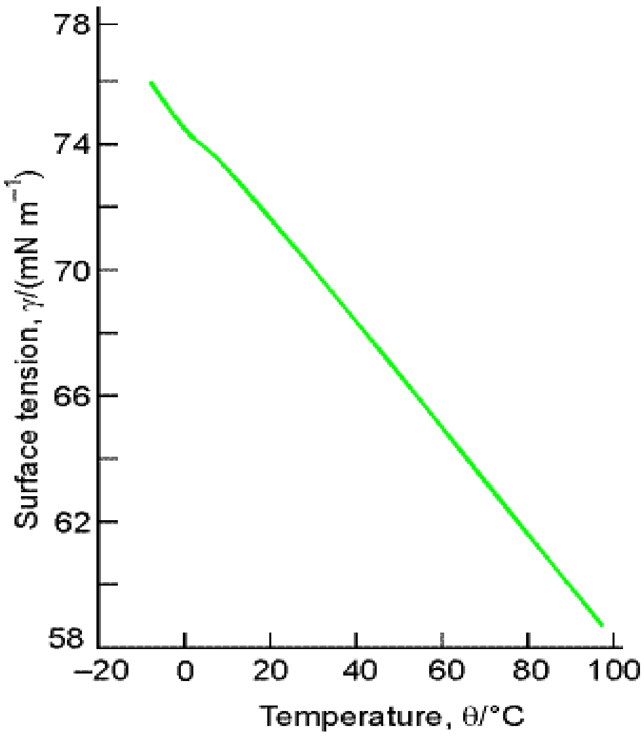
$$p_1^{(l)} = p_1^{(g)} - \frac{2\gamma}{r}$$

$$p_2^{(l)} = p_2^{(g)}$$



(a)

6.10 Capillary action



The variation of the surface tension of water with temperature.

$$\gamma = \frac{hrg\rho^{(l)}}{2}$$

This simple expression provides a reasonably accurate way of measuring the surface tension of liquids. Surface tension decreases with increasing temperature.

6.10 Capillary action

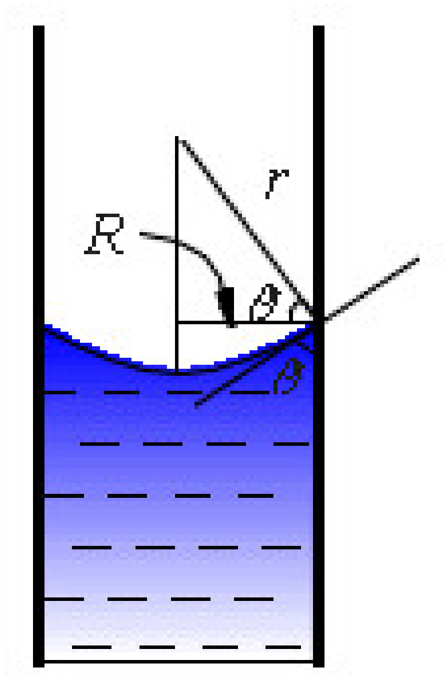
2). The contact angle

$$h = \frac{2\gamma}{rg\rho^{(l)}}$$

$$r = R / \cos\theta$$

$$\gamma = \frac{r\rho^{(l)}gh}{2}$$

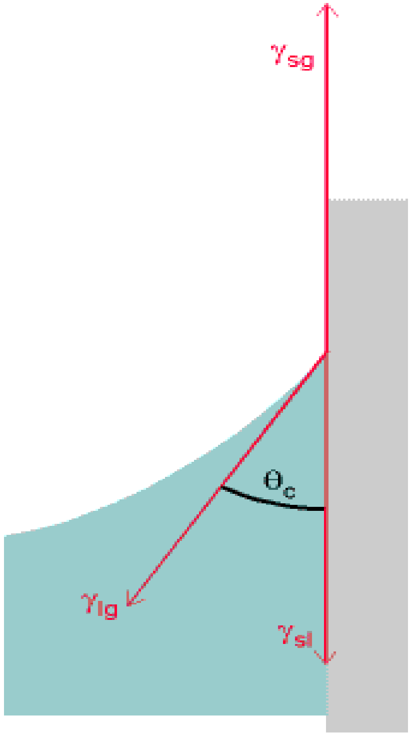
$$\gamma = \frac{R\rho^{(l)}gh}{2\cos\theta_c}$$



θ, contanct angle

6.10 Capillary action

2). The contact angle



The balance of forces that results in a contact angle, θ_c.

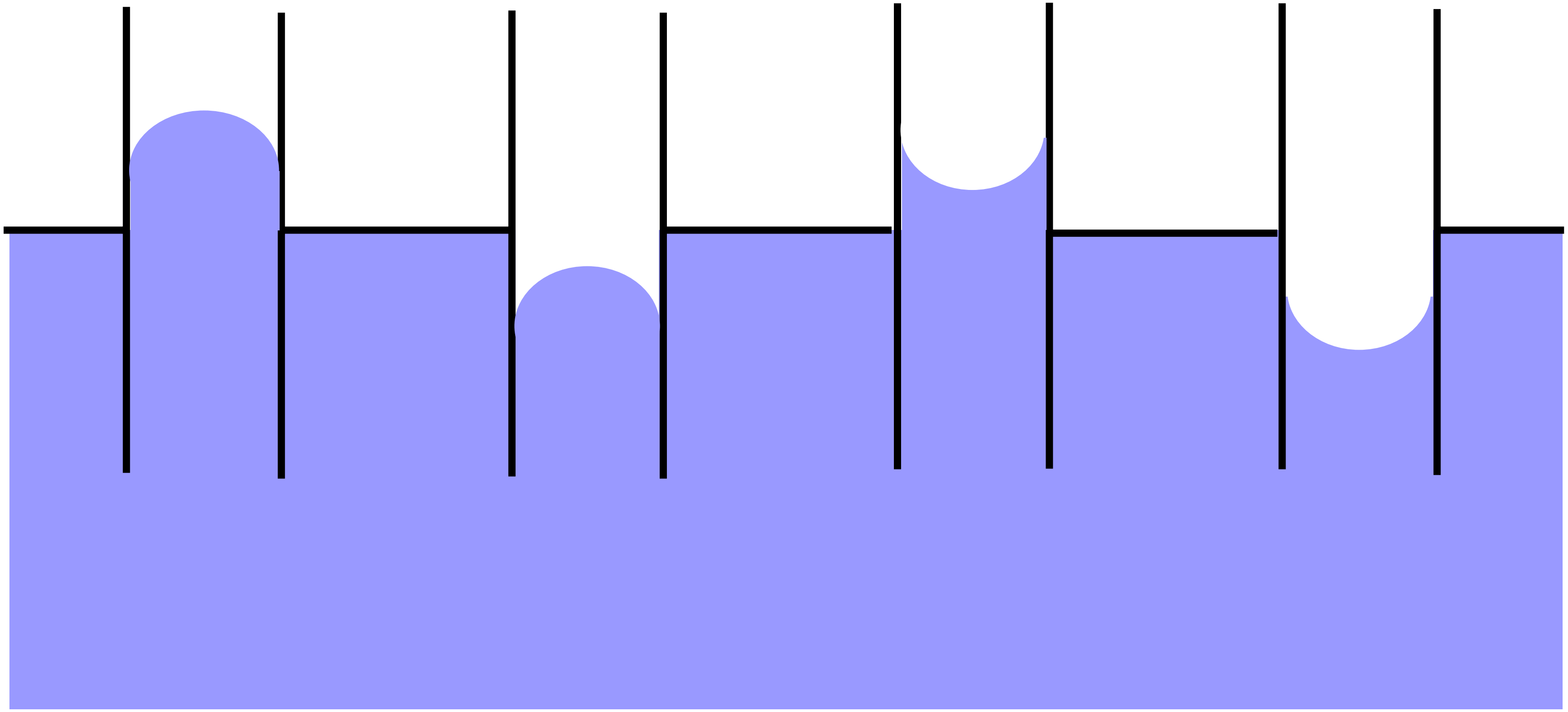
The origin of the contact angle can be traced to the balance of forces at the line of contact between the liquid and the solid. If the solid-gas, solid-liquid, and liquid-gas surface tensions are denoted γ_{sg}, γ_{sl} and γ_{lg}, respectively, in balance

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos\theta_c$$

$$\cos\theta_c = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}}$$

Examples

Identify which of the followings is(are) correct

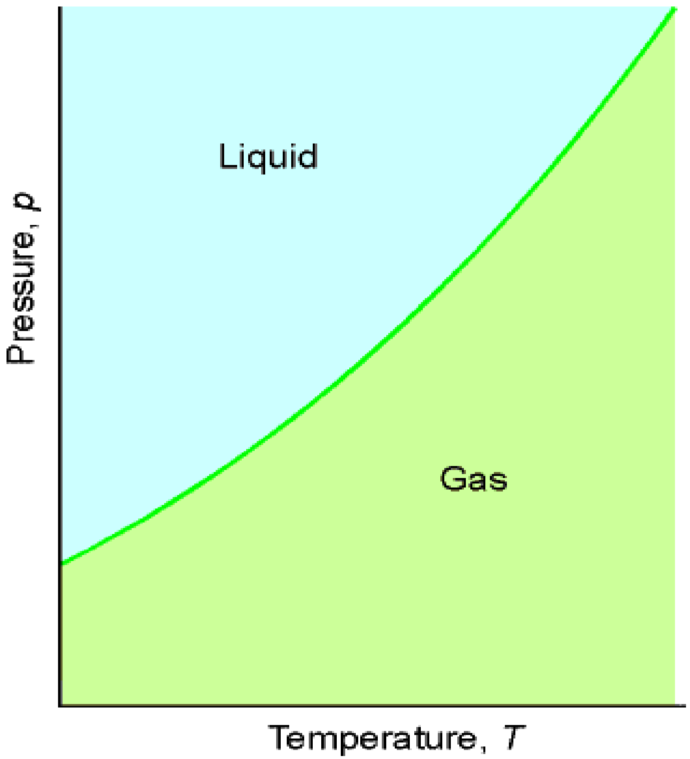


Examples

The vapor pressure of a liquid in the temperature range 200 K to 260 K was found to fit the expression $\ln(p/\mathrm{Torr}) = 18.361 - 3036.8/(T/\mathrm{K})$. Calculate the enthalpy of vaporization of the liquid.

Examples

From the Clausius-Clapeyron equation, we can obtain



$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}} H}{RT^2}$$

$$\int \mathrm{d}\ln p = \int \frac{\Delta_{\mathrm{vap}} H}{RT^2}\mathrm{d}T$$

$$\ln p = C - \frac{\Delta_{\mathrm{vap}} H}{RT}$$

In the equation, C is a constant.

Examples

$$\ln p = C - \frac{\Delta_{\mathrm{vap}} H}{RT}$$

$$\ln p = 18.361 - \frac{3036.8}{T}$$

$$-\frac{3036.8}{T/\mathrm{K}} = -\frac{\Delta_{\mathrm{vap}} H}{RT}$$

$$\Delta_{\mathrm{vap}} H = 3036.8R$$

$$= 8.314\,\mathrm{JK}^{-1}\mathrm{mol}^{-1} \times (3036.8\mathrm{K})$$

$$= 25.25 \times 10^{3}\,\mathrm{Jmol}^{-1} = 25.25\,\mathrm{kJmol}^{-1}$$

Examples

The boiling point of hexane is 69.0 ℃. Estimate

(a) its enthalpy of vaporization and

(b) its vapor pressure at 25 ℃ and 60 ℃.

Examples

(a) According to Trouton's rule: a wide range of liquids giving approximately the same standard entropy of vaporization,

$$\Delta_{\mathrm{vap}} S = 85\,\mathrm{JK^{-1}mol^{-1}}$$

$$\Delta_{\mathrm{vap}} S = \frac{\Delta_{\mathrm{vap}} H}{T_b}$$

$$\Delta_{\mathrm{vap}} H = (85\,\mathrm{JK^{-1}mol^{-1}}) \times T_{\mathrm{b}}$$

$$= (85\mathrm{JK^{-1}mol^{-1}}) \times (273.2 + 69.0)$$

$$= 29.1 \times 10^{3}\,\mathrm{Jmol^{-1}} = 29.1\mathrm{kJmol^{-1}}$$

Examples

(b) Use the Clausius-Clapeyron equation

$$\ln\frac{p_2}{p_1}=\frac{\Delta_{\text{vap}}H}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

□ At T_2=342.2K, p_2=1.00atm; thus at 25 ℃

$$\ln p_1=-\frac{29.1\times10^{3}\ \text{Jmol}^{-1}}{8.314\ \text{JK}^{-1}\text{mol}^{-1}}\times\left(\frac{1}{298.2\text{K}}-\frac{1}{342.2\text{K}}\right)$$

$$=-1.509$$

$$p_1=0.22\ \text{atm}$$

Examples

□ At 60 ℃, p_2=1.00atm

$$\ln p_1 = -\frac{29.1\times10^3\ \mathrm{Jmol}^{-1}}{8.314\ \mathrm{JK}^{-1}\mathrm{mol}^{-1}}\times\left(\frac{1}{333.2\mathrm{K}}-\frac{1}{342.2\mathrm{K}}\right)$$

$$= -0.276$$

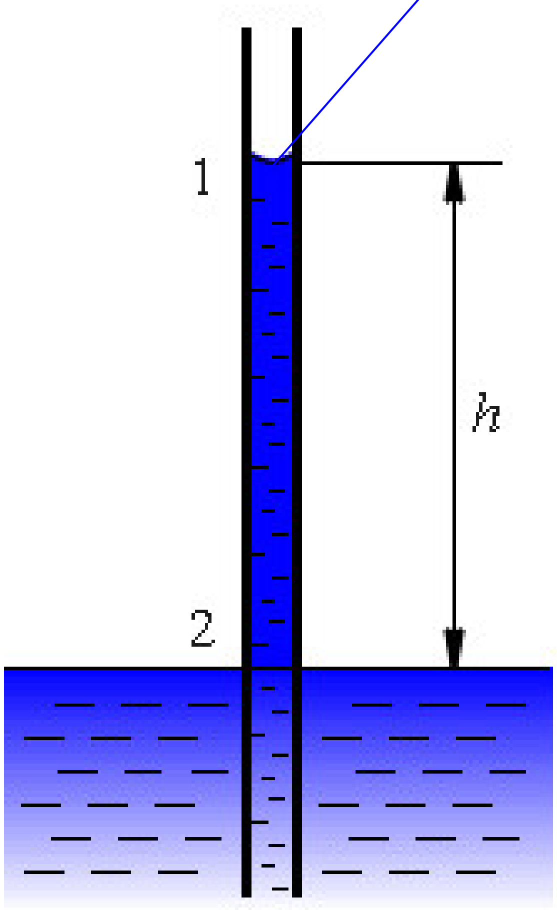
$$p_1 = 0.76\ \mathrm{atm}$$

Examples

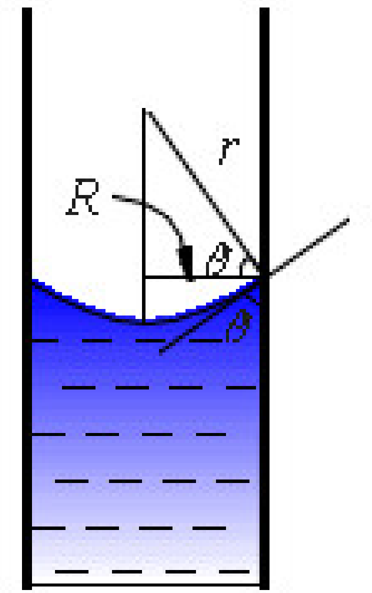
The contact angle for water on clean glass is close to zero. Calculate the surface tension of water at 30 ℃ given that at that temperature water climbs to a height of 9.11cm in a clean glass capillary tube of internal diameter 0.320 mm. The density of water at 30℃ is 0.9956 gcm^{-3}

Examples

$$p_1^{(l)} = p_1^{(g)} - \frac{2\gamma}{r}$$



(a)



(b)

$$p_\mathrm{l} - p_\mathrm{g} = (\rho_\mathrm{g} - \rho_\mathrm{l})gh$$

$$\approx -\rho_\mathrm{l} gh$$

$$p_\mathrm{l} - p_\mathrm{g} = -\frac{2\gamma}{r}$$

$$r = R/\cos\theta$$

$$-\frac{2\gamma}{R/\cos\theta} = -\rho_\mathrm{l} gh$$

$$\gamma = R\rho_\mathrm{l} gh/2\cos\theta$$

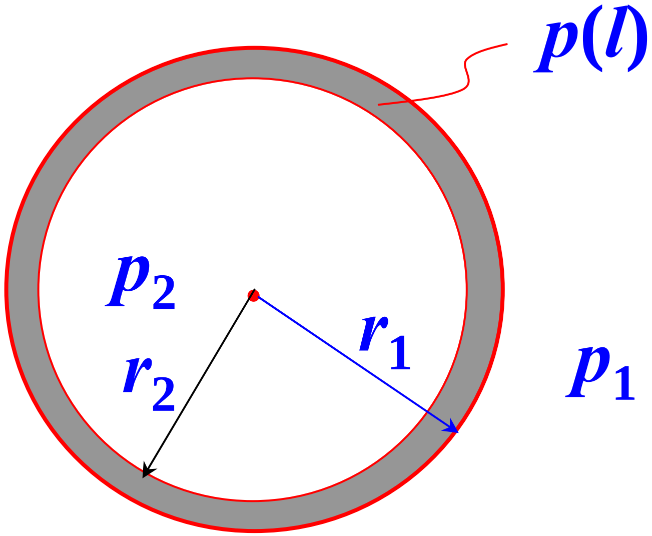
Examples

$$\gamma = R\rho_l gh/2\cos\theta$$

$$\gamma = (0.16\times10^{-3})\times(0.9956\times10^{3})\times9.81\times(9.11\times10^{-2})$$
$$/2\times\cos\theta$$
$$= 7.12\times10^{-2}\,\mathrm{Nm}^{-1}$$

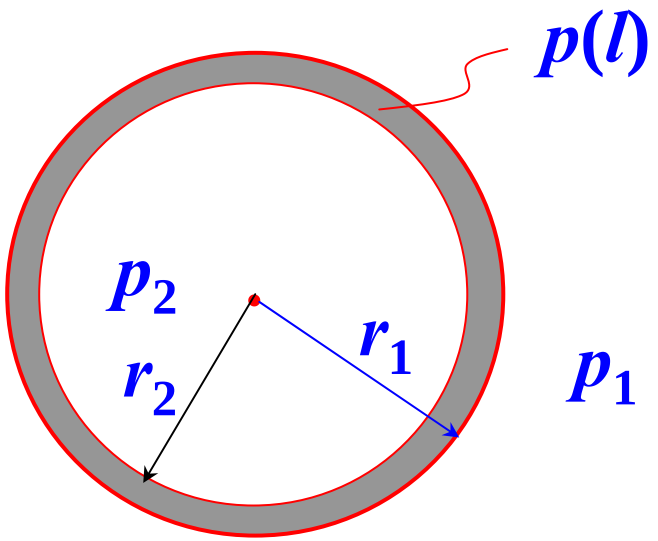
Examples

Calculate the difference between pressures inside and outside of the bubble in air with a radius 1 cm shown as the following figure. Given that the surface tension is 0.040Nm^{-1}



Examples

Answer:



Laplace equation gives that

$$p_{\text{in}} = p_{\text{out}} + \frac{2\gamma}{r}$$

For the outside

$$p(l) = p_1 + \frac{2\gamma}{r_1}$$

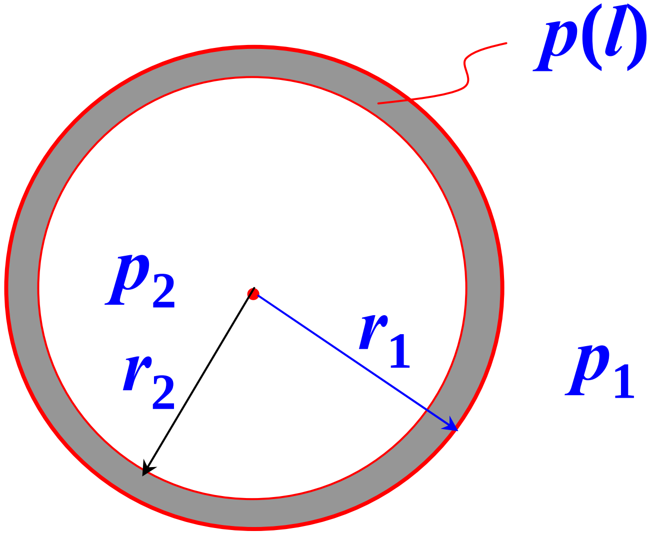
For the inside

$$p(l) = p_2 - \frac{2\gamma}{r_2}$$

Examples

It follows that

$$p(l) = p_2 - \frac{2\gamma}{r_2} = p_1 + \frac{2\gamma}{r_1}$$



$$p_2 - p_1 = \frac{2\gamma}{r_1} + \frac{2\gamma}{r_2}$$

$$\approx 2 \times \frac{2\gamma}{r}$$

$$= \frac{4\gamma}{r}$$

$$\Delta p = \frac{40.0400\ \mathrm{Nm}^{-1}}{1 \times 10^{-2}\ \mathrm{m}}$$

$$= 16.0\mathrm{Pa}$$

Part 1: Equilibrium

1. The properties of gases
2. The First Law: the concepts
3. The First Law: the machinery
4. The Second Law: the concepts
5. The Second Law: the machinery
6. Physical transformations of pure substances
7. Simple mixtures
8. Phase diagrams
9. Chemical equilibrium
10. Electrochemistry