
Physical Transformations of Pure Substances

Chapter 6 of Atkins

Sections 6.1-6.6 (6th, 7th Eds.), Sections 4.1-4.6 (8th Ed.)

Phase Diagrams

Stabilities of Phases

Phase Boundaries

Three Typical Phase Diagrams

Phase Stability and Phase Transitions

Thermodynamic Criterion of Equilibrium

Dependence of Stability on the Conditions

Location of Phase Boundaries

Last updated: Nov. 10, 2008, slide 5 repaired, slide 21 fixed.

Phase Transformations

We now move from some of the relatively abstract concepts of the first five chapters to some direct applications of thermodynamics: *Apply the laws of thermodynamics to physical transformations of pure substances*

How do we know the phase of a substance at a given **pressure** and **temperature**?

The Gibbs energy can give us the answer to this question:

Spontaneous processes have negative changes in Gibbs free energy

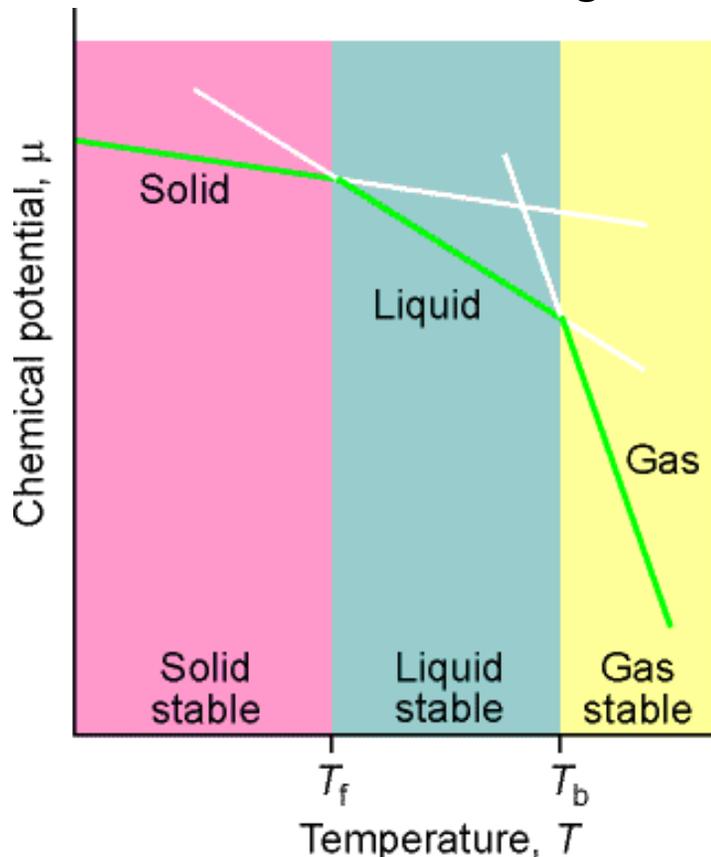
For example, if you want to know the most stable phase of water at a given pressure and temperature, you can calculate the Gibbs energies for each of the phases, compare them and pick the lowest one

Chemical potentials are equivalent to **molar** Gibbs energies for pure substances, so *the phase with the lowest chemical potential will be the most stable phase*

Stabilities of Phases

Phase: A form of matter that is uniform throughout in both chemical composition and physical state

Phase Transition: **Spontaneous conversion** of one phase into another, occurring at a characteristic temperature for a given pressure



Consider water at $p = 1$ atm:

Ice is stable phase when $T < 0$

$\mu_{\text{ice}} < \mu_{\text{liquid water}}$ when $T < 0$

Liquid water is stable phase when $T > 0$

$\mu_{\text{ice}} > \mu_{\text{liquid water}}$ when $T > 0$

Transition Temperature, T_{trs} :

Temperature when chemical potentials are equal; for example, $\mu_{\text{ice}} = \mu_{\text{liquid water}}$ at $T = 0$

Rates of Phase Transitions

Distinguish between:

Spontaneity of transition

Thermodynamics may predict the spontaneity of the physical transformation, but not the rate at which it occurs

Rate of transition

Kinetics predicts the rate at which a transition occurs, but not the spontaneity

Consider the phase transition from diamond to graphite:

Normal pressure and temperature, $\mu_{\text{diamond}} > \mu_{\text{graphite}}$

For change to take place, C atoms must exchange positions, which is an incredibly **slow process for solids** (except at high temperatures)

In gases and liquids, these changes can take place rapidly, but in solids, **thermodynamic instability** may be inherent in the system

Metastable phases: Thermodynamically unstable phases that persist due to kinetic hindrance

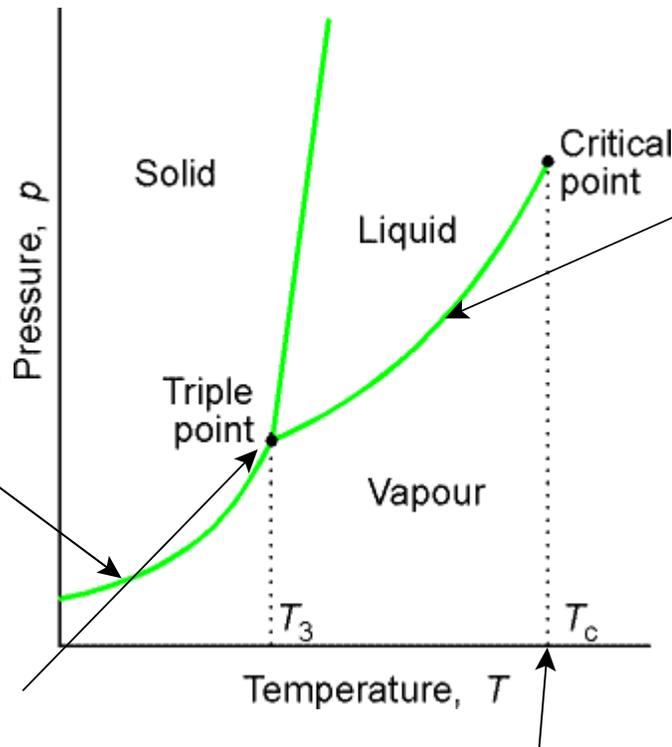
Phase Boundaries

Phase Diagram: Shows regions of pressure and temperature where phases are thermodynamically stable

Sublimation Vapour Pressure

Pressure of gas in equilibrium with solid phase

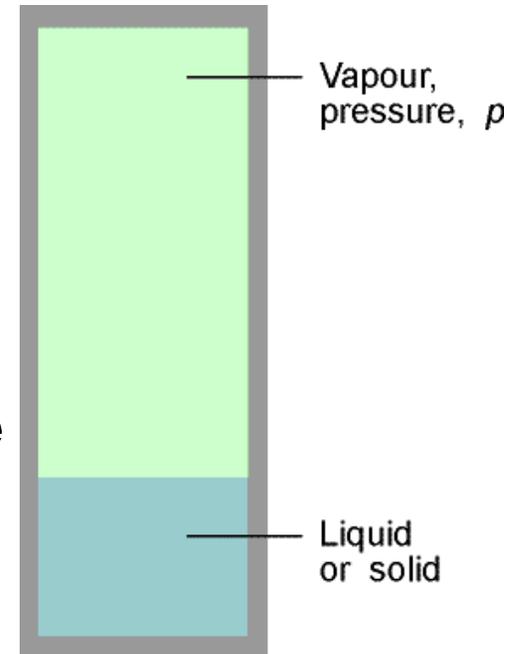
Phase Boundaries separate regions and show p and T where two phases exist in equilibrium



Triple Point Critical Temperature

Vapour Pressure

Pressure of a gas in equilibrium with the liquid phase



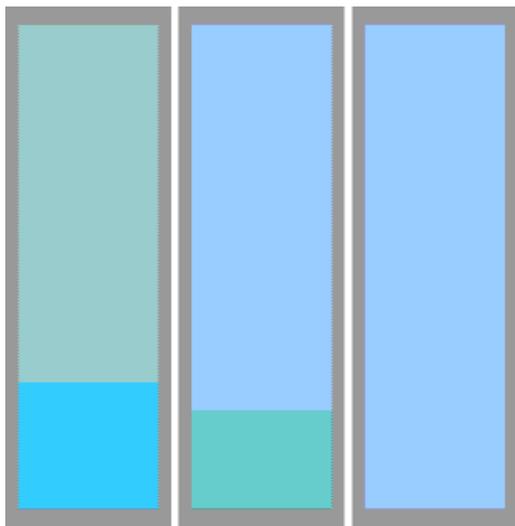
Vapour pressures increase with increasing T , as the Boltzmann distribution populates the higher energy states with increasing temperature

Critical Points and Boiling Points

In an **open vessel**, at the temperature where the vapour pressure is equal to the external pressure, free vapourization occurs throughout the liquid, and vapour can expand freely into the surroundings. **Free vapourization** is known as **boiling**

The **normal boiling point**, T_b , is the temperature of free vapourization at a pressure of 1.0 atm

The **standard boiling point** is the temperature of free vapourization at a pressure of 1.0 bar (0.987 atm) (e.g., water: 99.6°C for $T_b = 100^\circ\text{C}$)



(a)

(b)

(c)

In a **closed vessel**, boiling does not occur - rather the vapour pressure and density of the vapour increase with increasing temperature

(a) equilibrium, (b) increasing density & (c) two densities equal, surface btw. phases disappears

Critical temperature, T_c and **critical pressure**, p_c : where interphase surface disappears

Supercritical fluid: fills container and interface no longer exists (figure c)

Melting Points and Triple Points

The temperature at a specified pressure where the liquid and solid phases coexist in equilibrium is called the **melting temperature** (or **freezing temperature** or **fusion temperature**)

The **normal freezing point**, T_f , is the temperature of freezing at a pressure of 1.0 atm (for water, $T_f = 0\text{ }^\circ\text{C}$)

The **standard freezing point** is the temperature of freezing at a pressure of 1.0 bar (0.987 atm) (negligibly different from T_f)

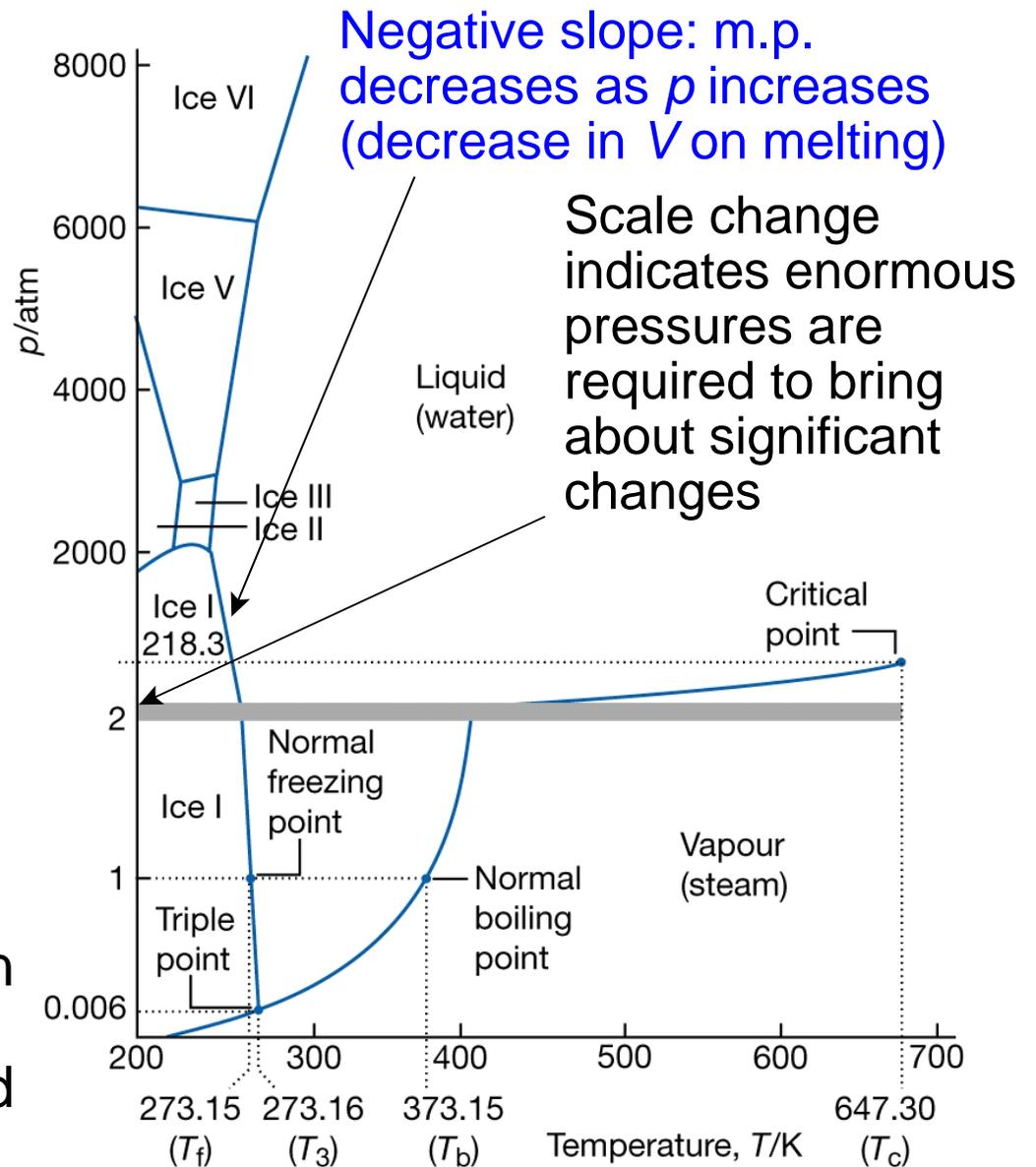
The point where all three phases exist in equilibrium is called the **triple point**, T_3 (three phase boundaries meet)

- T_3 occurs at a specific temperature and pressure which are characteristic of a substance
- T_3 marks lowest pressure in which a liquid phase of a substance can exist

Example: Water, $T_3 = 273.16\text{ K}$ and 611 Pa (6.11 mbar, 4.58 Torr)

Phase Diagram of Water

- The liquid-vapour boundary shows variation of vapour pressure with temperature
- The solid-liquid boundary shows variation of melting point with temperature
- **Glacier motion** may result from decrease in m.p. with increasing p
- At extremely high pressures, different phases of ice come into existence, as bonds between molecules are modified by huge stresses
- Multiple triple points exist within the diagram other than the lowest where vapour, liquid and ice I coexist



Cat's Cradle & Ice IX

Kurt Vonnegut's 1962 novel "*Cat's Cradle*" describes the irresponsibility of nuclear scientists in a playful manner. The focus is on the fictional Dr. Hoenikker, the inventor of the atomic bomb.



We further learn that on the night of his death, years later, he was again "playing around"--in the kitchen this time, with some water and bits of ice. With his characteristically pure-science approach ("Why doesn't someone do something about mud?" the Marine Corps general had asked him) he has isolated crystals of ice in such a way that water can now be caused to freeze at a relatively high temperature. "Ice-9" it is called. The family dog laps at a bowl of water which has been touched with a piece of Ice-9 and is promptly frozen stiff.

Dr. Breed was mistaken about at least one thing: there was such a thing as ice-nine.

And ice-nine was on earth.

Ice-nine was the last gift Felix Hoenikker created for mankind before going to his just reward.

He did it without anyone's realizing what he was doing. He did it without leaving records of what he'd done.

True, elaborate apparatus was necessary in the act of creation but it already existed in the Research Laboratory. Dr. Hoenikker had only to go calling on Laboratory neighbors--borrowing this and that, making a winsome neighborhood nuisance of himself--until, so to speak, he had baked his last batch off brownies.

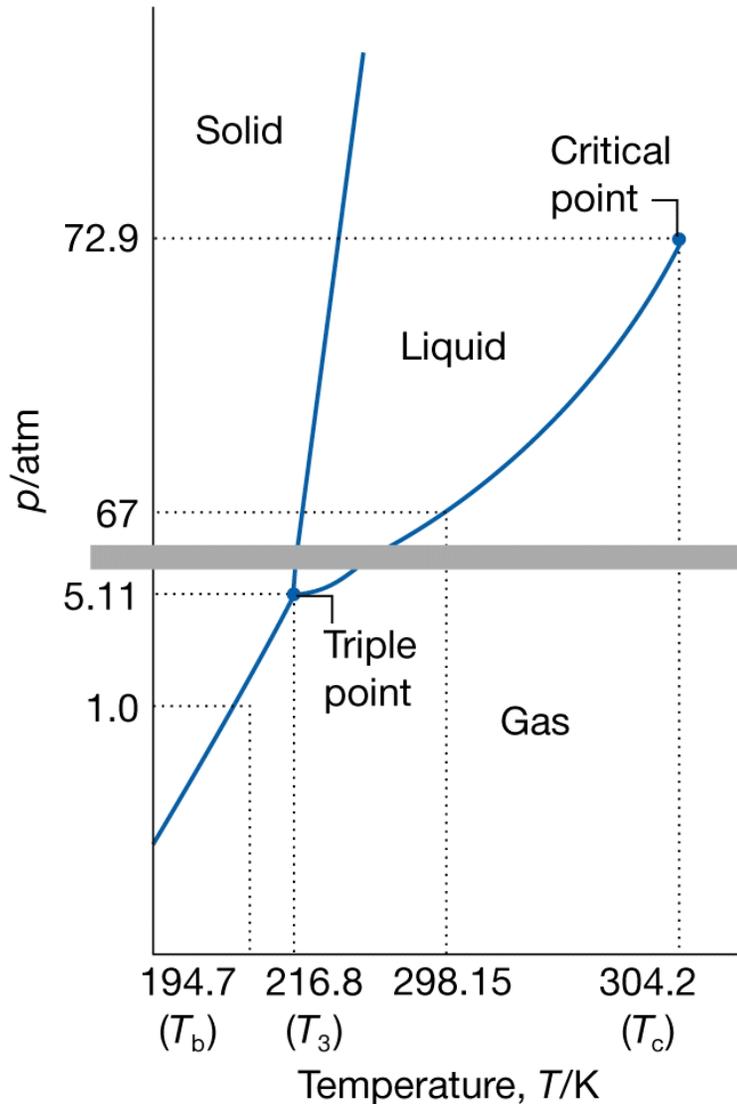
He had made a chip of ice-nine. It was blue-white. It had a melting point of one-hundred-fourteen-point-four-degrees Fahrenheit.

Felix Hoenikker had put the chip in a little bottle; and he put the bottle in his pocket. And he had gone to his Cottage on Cape Cod with his three children, there intending to celebrate Christmas.

Angela had been thirty-four. Frank had been twenty-four. Little Newt had been eighteen. The old man had died on Christmas Eve, having told only his children about ice-nine.

His children had divided the ice-nine among themselves.

CO₂, Fire Extinguishers & Coffee



- **Positive slope of solid-liquid boundary** is characteristic of most substances (m.p. increases as pressure is increased)
- Triple point lies above 1 atm, implying that liquid CO₂ cannot exist at normal pressures (solid sublimates at normal pressures, hence the name, “**dry ice**”)
- To obtain liquid CO₂, $p = 5.11$ atm is the minimum. For a cylinder of CO₂(l) at 25°C, the pressure of the gas must be greater than 67 atm - gas comes out of a Joule-Thomson throttle, emerging into $p = 1$ atm, condenses into a **snow-like solid**
- Supercritical CO₂ (highly compressed) is used in supercritical fluid chromatography which separates lipids and phospholipids, and fuel oils into components; also, it is used to **decaffeinate coffee**

Supercritical fluid: CO₂

Supercritical fluids (notably, CO₂, $T_c = 31.1$ °C, thermally labile organics) have wide ranging industrial applications, including:

- decaffeination of coffee
- extraction of edible oils (e.g., soybeans, lemon oil)
- extraction of chemotherapeutic agents from plants
- treatment of waste streams (PCBs, dioxin, petroleum byproducts)
- deoiling of greasy foods

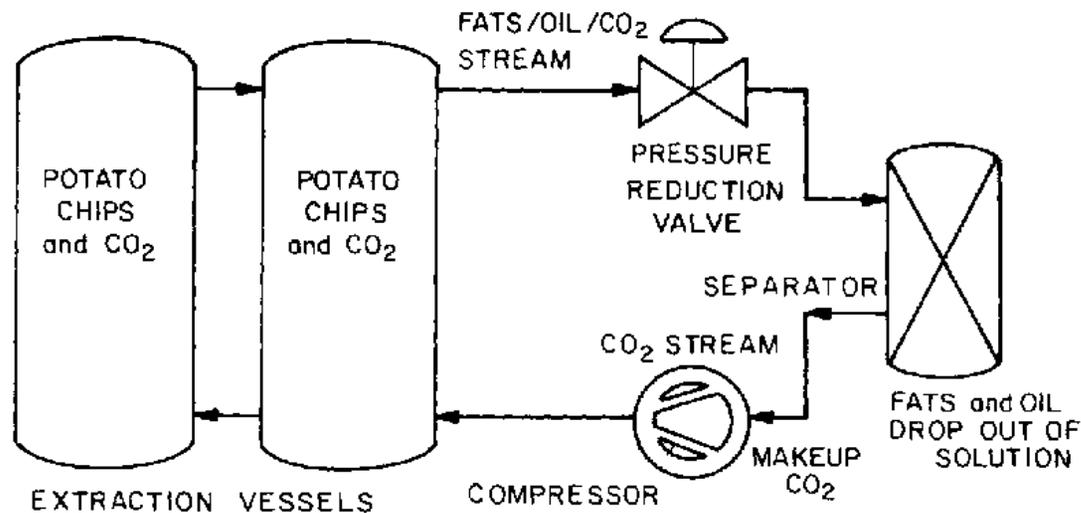
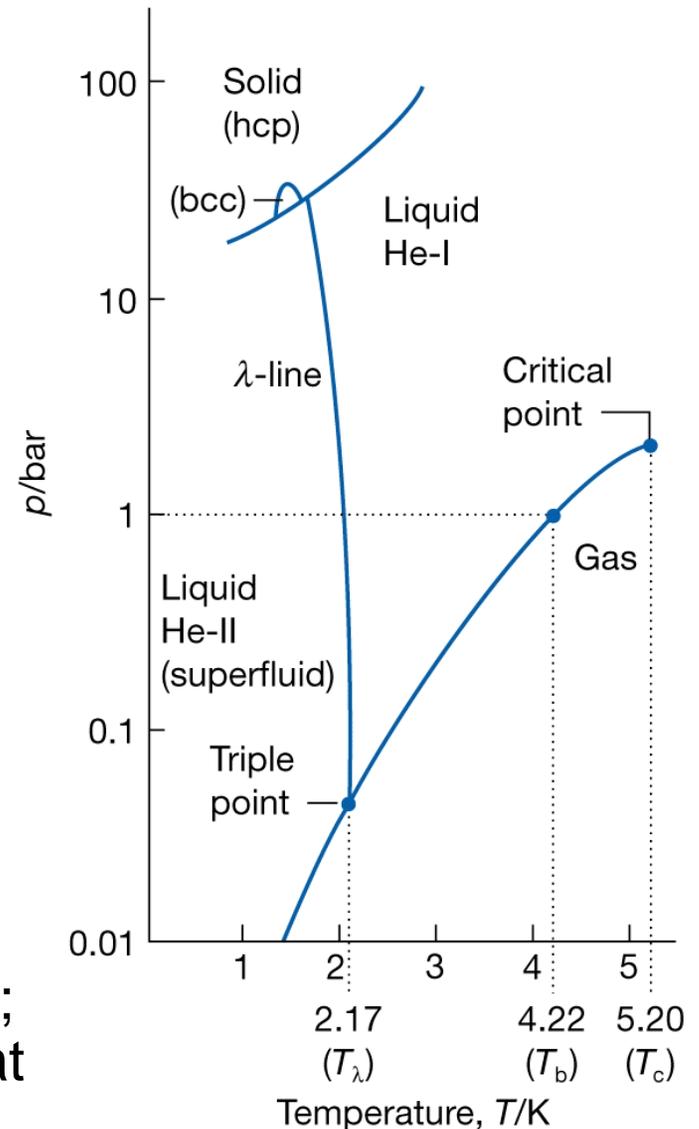


Figure 10.6 Schematic diagram of the process for deoiling potato chips with supercritical carbon dioxide.

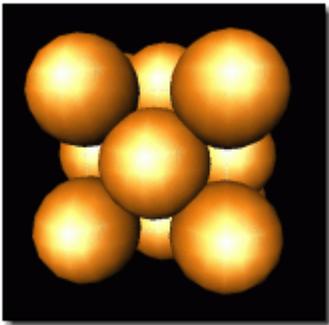
Phase Diagram of Helium (^4He)

- At low temperatures, helium behaves unusually - solid and gas are never in equilibrium: He atoms are so light that they vibrate with high amplitude motions which “shake the solid apart”
- Solid helium can only be obtained at low temperature and very high pressure - hcp and bcc denote **hexagonal close packing** and **body-centred cubic packing**
- The λ -line marks a special phase transition where heat capacity becomes infinite, marking the fluid-**superfluid** transition of liquid Helium
- The He-II liquid phase is a **superfluid**, as it flows without any viscosity
- ^4He and ^3He have different phase diagrams; in fact, the entropy of ^3He (l) is less than that of ^3He (s), so **melting is exothermic**

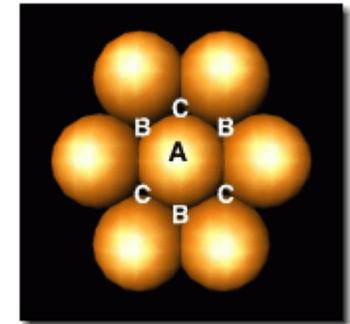


Close Packing in Solids

In a solid, atoms pack together in different arrangements to occupy as much space as possible - **close packing**

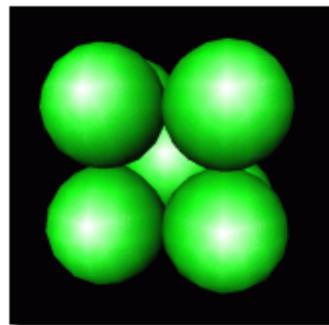
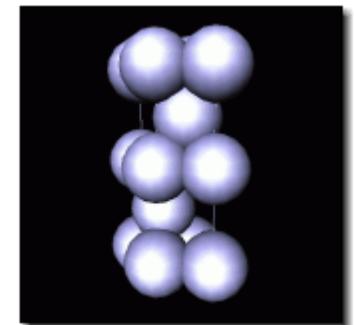


Each atom A is surrounded by six other A atoms in one layer, atoms are then piled on top in the B and C “holes”



Atoms that pack in the arrangement ABC.ABC.ABC... are said to have **cubic close packing (ccp)** which is also called **face-centred cubic (fcc)** packing (e.g., gold)

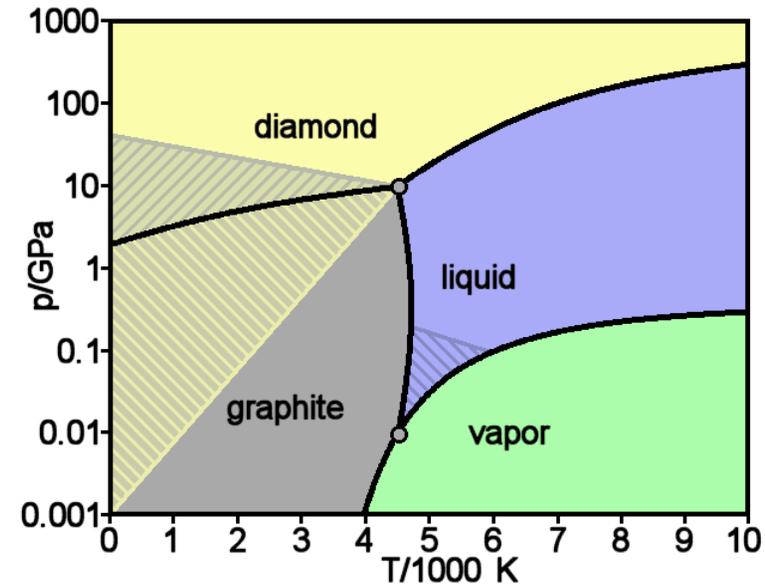
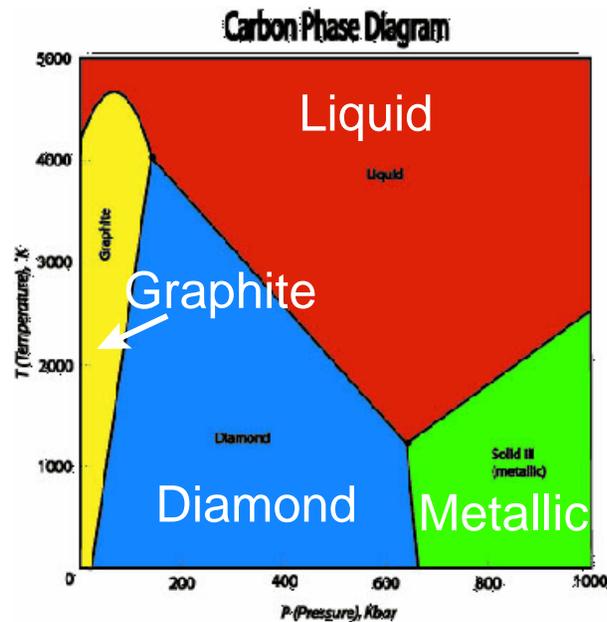
Packing in the arrangement AB.AB or AC.AC results in **hexagonal close packing (hcp)** - there is often competition between ccp and hcp phases, dependent upon long range forces of the atoms (e.g., low temp Na)



The **body-centred cubic (bcc)** packing arrangement is slightly less close packed than fcc and hcp, with one atom at the centre, and other atoms at the corners - it is often the high temperature form of metals that are close-packed at lower temperatures (e.g., iron either ccp or bcc, heating)

Diamonds are not forever?

Carbon can exist in several different solid phases, as represented by the phase diagrams below:

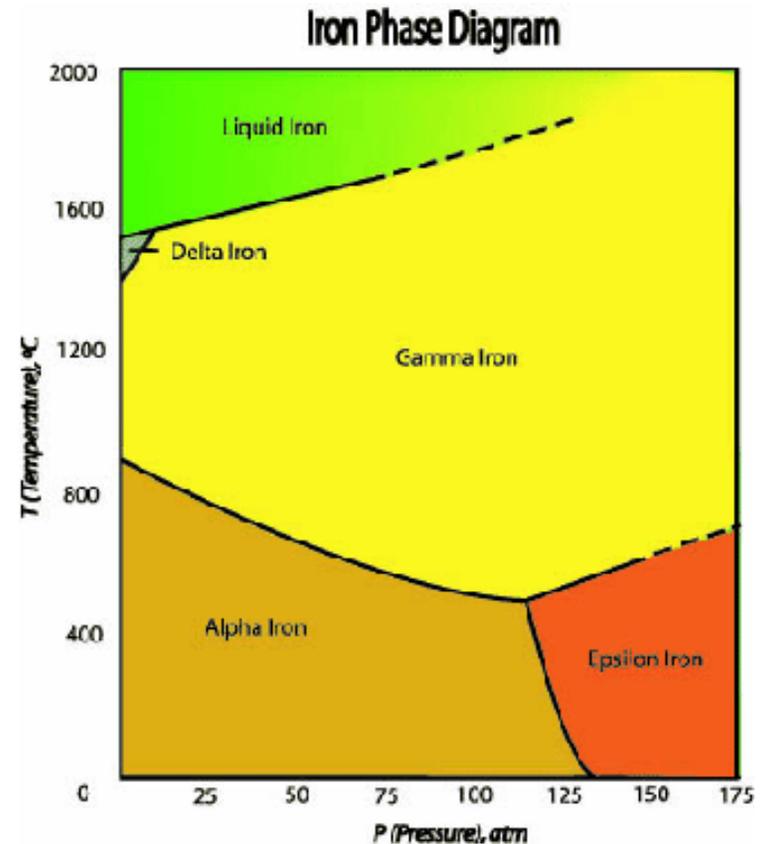
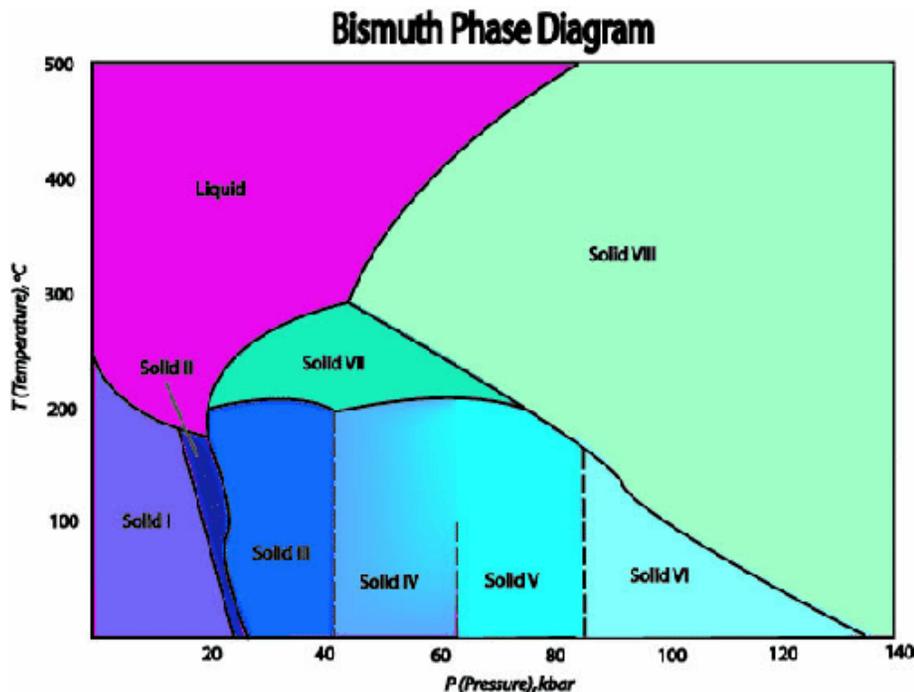


The left p - T diagram shows the high- T high- p “metallic” phase of carbon, whereas the right T - p diagram shows the high- T low p vapour phase. Hatched regions indicate “**metastable**” phases, where both phases can co-exist.

Carbon also has a pure allotropic forms known as buckminsterfullerenes or buckyballs (C_{60} , C_{70} , etc.), which are produced via chemical reactions.

Phase diagrams of some metals

Bismuth and iron have complex one-component phase diagrams

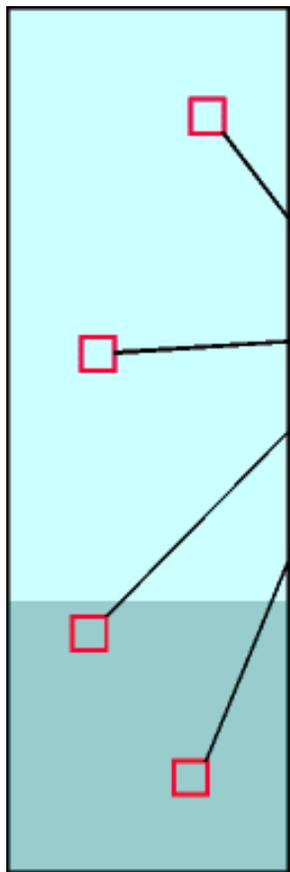


- Bi (and Sb) has a similar solid-liquid volume anomaly to H₂O
- Fe apparently has a triple point where α , γ and ϵ iron all exist simultaneously

Phase Stability and Phase Transitions

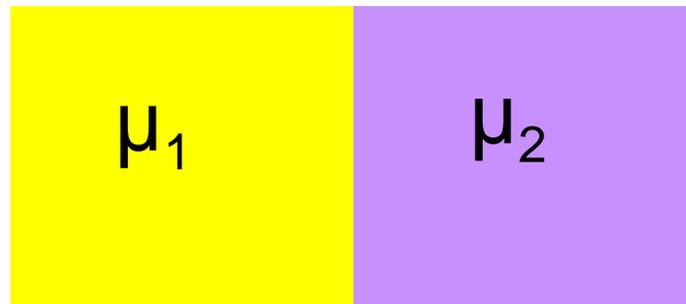
The **thermodynamic criterion of equilibrium** is:

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



For example, when solid and liquid phases are in equilibrium, neither has a higher chemical potential (same throughout the solid and the liquid)

Same
chemical
potential



If *amount* dn is transferred from 1 to 2, Gibbs energy changes by $-\mu_1 dn$ in location 1, and by $+\mu_2 dn$ in location 2

$$dG = (\mu_2 - \mu_1) dn$$

If $\mu_1 > \mu_2$, ΔG is negative, process is spontaneous

If $\mu_1 = \mu_2$, no change in ΔG , system at equilibrium

If $\Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0$, system at equilibrium

Temperature Dependence of Phase Stability

Temperature dependence of Gibbs energy is expressed in terms of entropy, $(\partial G/\partial T)_p = -S$. Since the chemical potential of a pure substance is the same as the molar Gibbs energy, we can write

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$

As T increases, μ decreases and $S_m > 0$, so: slope of μ vs. T is negative (see the next slide)

Plot of μ vs. T is steeper for gases than liquids, since the $S_m(g) > S_m(l)$.
For solids and liquids, usually $S_m(s) < S_m(l)$

Solids and Liquids:

Steep negative slope of $\mu(l)$ falls below $\mu(s)$ when the temperature is high enough (liquid becomes stable phase and solid melts)

Liquids and Gases:

$\mu(g)$ plunges downwards as temperature is raised ($S_m(g)$ high!), so the gas is the stable phase and the liquid vapourizes

Melting Response to Applied Pressure

Most substances melt at a higher temperature when subjected to pressure (the pressure prevents the formation of a less dense liquid phase) - an exception is water, with $\rho(l) > \rho(s)$ [i.e., $V_m(s) > V_m(l)$]

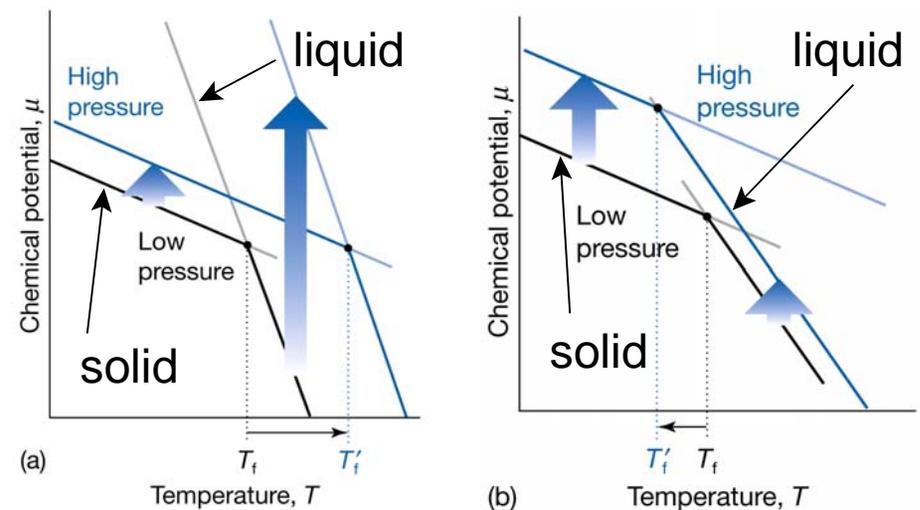
The variation of chemical potential with pressure is

$$\left(\frac{\partial \mu}{\partial p} \right)_T = V_m$$

so, the slope of chemical potential vs. pressure is equal to molar volume

Increase in pressure raises the chemical potential of most pure substances, because V_m must be greater than zero

In (a), the **freezing temperature increases**, and in (b) the **freezing temperature is lowered** (these are plots of negative entropy)



$$V_m(s) < V_m(l)$$

$$V_m(s) > V_m(l)$$

Pressure and Chemical Potential

Example: Calculate the effect of chemical potentials of ice and water of increasing the pressure from 1.00 bar to 2.00 bar at 0°C. The density of ice is $\rho = 0.917 \text{ g cm}^{-3}$, and of water is $\rho = 0.999 \text{ g cm}^{-3}$

$\Delta\mu = V_m\Delta p$ for change in chemical potential of an incompressible substance when pressure is changed by Δp ; thus,

$$\Delta\mu = \frac{M\Delta p}{\rho}$$

$$\Delta\mu(\text{ice}) = \frac{(1.802 \times 10^{-2} \text{ kg mol}^{-1}) \times (1.00 \times 10^5 \text{ Pa})}{917 \text{ kg m}^{-3}} = +1.97 \text{ J mol}^{-1}$$

$$\Delta\mu(\text{water}) = \frac{(1.802 \times 10^{-2} \text{ kg mol}^{-1}) \times (1.00 \times 10^5 \text{ Pa})}{999 \text{ kg m}^{-3}} = +1.80 \text{ J mol}^{-1}$$

$\mu(\text{ice})$ rises more sharply than $\mu(\text{water})$, so if they are at equilibrium at 1.00 bar, there is a tendency for ice to melt at 2.00 bar

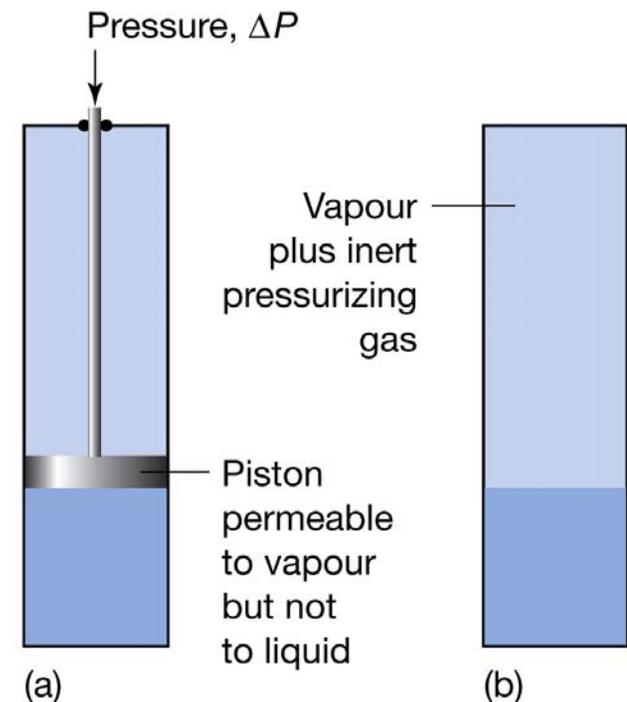
(This is the reason applying additional pressure to ice at constant temperature results in melting to liquid phase!)

Applied Pressure and Vapour Pressure

When pressure is applied to a condensed phase, the vapour pressure rises (molecules are squeezed out and escape as a gas)

Pressure can be exerted on the condensed phase: (a) mechanically or (b) subjecting it to an inert pressurizing gas

In case (b), vapour pressure is the partial pressure of the vapour in equilibrium with the condensed phase - this is the **partial vapour pressure** of the substance (it is possible that some of the inert gas can dissolve in the condensed phase if it is a liquid, or perhaps **solvate** some of the liquid molecules but we will not treat these complications)



The relationship between vapour pressure, p , after an applied pressure change of ΔP , and vapour pressure p^* , in absence of additional pressure, is:

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

Vapour pressure increases when pressure acting on condensed phase increases

Justification[†]

At equilibrium, $\mu(l) = \mu(g)$; so, any change that preserves equilibrium, the resulting change in $\mu(l)$ must be equal to that in $\mu(g)$ ($d\mu(l) = d\mu(g)$)

When pressure P on liquid is increased by dP , $d\mu(l) = V_m(l) dP$, and $d\mu(g) = V_m(g) dp$ ($dp =$ change in vapour pressure). If vapour is a perfect gas, $V_m(g) = RT/p$, and

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

If changes in chemical potentials of vapour and liquid are equated:

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

When no additional pressure is applied to the liquid, the pressure P experienced by the liquid is equal to the normal vapour pressure, p^* ; so $P = p^*$ and $p = p^*$ as well. When there is additional vapour pressure ΔP on the liquid, $P = p + \Delta P$. The effect on vapour pressure is so small, in $p - p^* + \Delta P = \Delta P$.

$$RT \int_{p^*}^p \frac{dp}{p} = \int_{p^*}^{p + \Delta P} V_m(l) dP \qquad RT \ln \left(\frac{p}{p^*} \right) = V_m(l) \Delta P$$

rearrange, q.e.d.

Estimating Effect of Pressure

Example: Derive an expression from the equation below that is valid for small changes in vapour pressure and calculate the fractional increase of vapour pressure of water for an increase in pressure of 10 bar @ 25°C

$$p = p^* e^{V_m \Delta P / RT} \quad e^x = 1 + x + x^2/2! + x^3/3! + \dots, \text{ so if } x \ll 1, e^x \approx 1 + x$$

If $V_m \Delta p / RT \ll 1$, then exponential function on RHS is ca. $1 + V_m \Delta p / RT$

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

rearranging:

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

For water, $\rho = 0.997 \text{ g cm}^{-3}$ at 25°C and $V_m = 18.1 \text{ cm}^3 \text{ mol}^{-1}$

$$\frac{V_m \Delta P}{RT} = \frac{(1.81 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}) \times (1.0 \times 10^6 \text{ Pa})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = 7.3 \times 10^{-3}$$

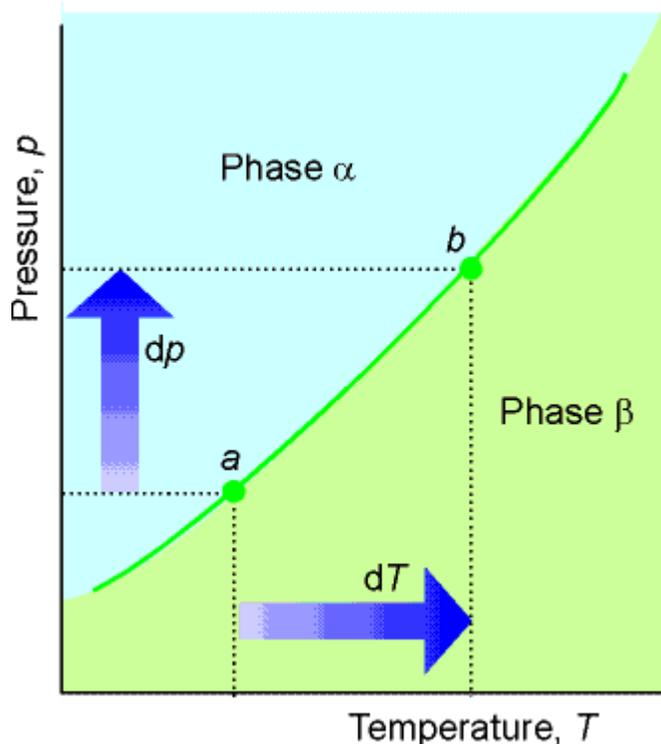
Since $V_m \Delta P / RT \ll 1$, so $(p - p^*) / p^* = 7.3 \times 10^{-3}$, increase of 0.73 %

Location of Phase Boundaries

Locations of phase boundaries are found by recognizing that when two phases are in equilibrium, chemical potentials are equal (phase α and β):

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

Solve the equation for p in terms of T to get the boundary equation



When pressure is applied to a system in which the two phases are in equilibrium (at a) the equilibrium is disturbed.

It can be restored by increasing the temperature (moving the system to state b)

So, there is a relationship between dp and dT , ensuring that the system stays in equilibrium as each variable is changed

Slopes of Phase Boundaries

p and T are changed infinitesimally such that two phases stay in equilibrium with one another - chemical potentials are initially equal, and remain equal after these changes (i.e., $d\mu_\alpha = d\mu_\beta$). For each phase:

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

thus,

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

hence,

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

which rearranges to give the **Clapeyron equation**:

$$\frac{dp}{dT} = \frac{\Delta_{\text{trs}} S}{\Delta_{\text{trs}} V}$$

where $\Delta_{\text{trs}} S = S_{\beta,m} - S_{\alpha,m}$ and $\Delta_{\text{trs}} V = V_{\beta,m} - V_{\alpha,m}$ are entropy and volume of the transition (exact expression for the slope of a phase boundary - applies to phase equilibrium of any pure substance)

Solid-Liquid Boundary

Melting (fusion) has an enthalpy change $\Delta_{\text{fus}}H$ occurs at T . Molar entropy at melting at T is $\Delta_{\text{fus}}H/T$, and we write the **Clapeyron equation** as

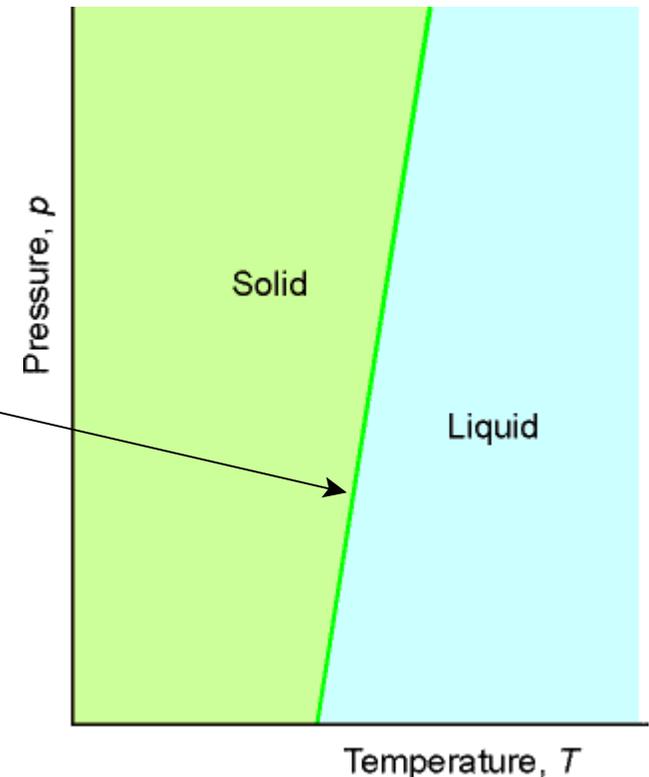
$$\frac{dp}{dT} = \frac{\Delta_{\text{fus}}H}{T \Delta_{\text{fus}}V}$$

$\Delta_{\text{fus}}V$ is change in molar volume on melting

Enthalpy of melting is positive (except ^3He) and volume change is usually +ve and small, so dp/dT is steep and positive

Formula for boundary is obtained by integration assuming that $\Delta_{\text{fus}}H$ and $\Delta_{\text{fus}}V$ are constant (very small changes):

$$\int_{p^*}^p dp = \frac{\Delta_{\text{fus}}H}{\Delta_{\text{fus}}V} \int_{T^*}^T \frac{dT}{T}$$



Solid-Liquid Boundary, 2

After integration, an approximate equation of the solid-liquid phase boundary is written as

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

When T is close to T^* (the melting temperature when pressure is p^*)

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

because $\ln(1+x) \approx x$ when $x \ll 1$, we can rewrite the above equation:

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

Plotting this equation as a function of T yields a steep straight line

Liquid-Vapour Boundary

Entropy of vapourization at temperature T is equal to $\Delta_{\text{vap}}H/T$

The **Clapeyron equation** for the liquid-vapour boundary is

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

$\Delta_{\text{vap}}H$ is positive, $\Delta_{\text{vap}}V$ is large and positive, so dp/dT is positive, but not as steep a slope as for the solid-liquid boundary:

dT/dp is large, boiling temperature is more responsive to pressure than the freezing temperature

To estimate the size of the effect of increasing p on the b.p. of liquids:

$$\Delta_{\text{vap}}V = V_{\text{m}}(\text{g}) - V_{\text{m}}(\text{l}) \approx V_{\text{m}}(\text{g}), \quad (\text{since } V_{\text{m}}(\text{g}) \gg V_{\text{m}}(\text{l}))$$

$$\frac{dp}{dT} = \frac{85 \text{ J K}^{-1} \text{ mol}^{-1}}{25 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} \text{ K}} = 3.4 \times 10^3 \text{ Pa K}^{-1}$$

This is 0.034 atm K^{-1} , so $dT/dP = 30 \text{ K atm}^{-1}$ (+0.1 atm pressure change alters the boiling point by approximately +3 K)

Liquid-Vapour Boundary, 2

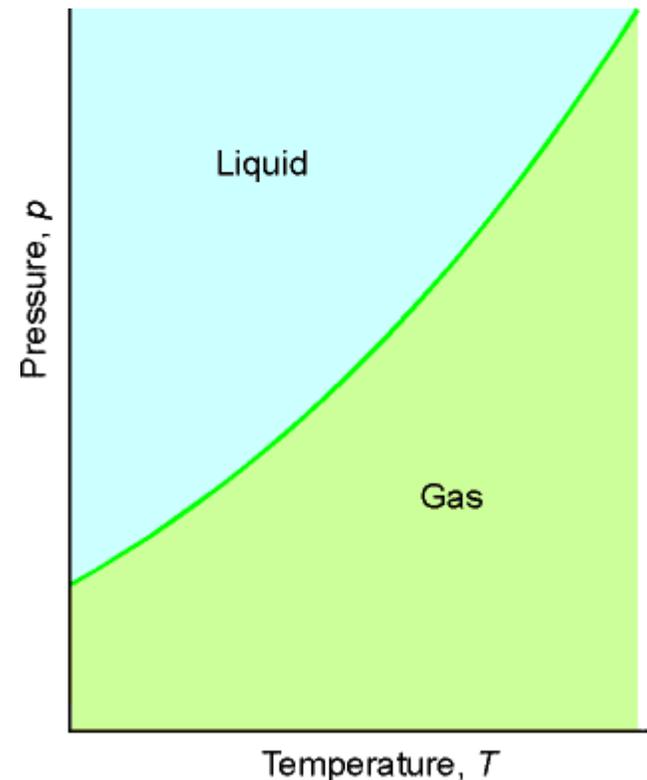
Since $V_m(g) \gg V_m(l)$, $\Delta_{\text{vap}} V \approx V_m(g)$. If gas behaves perfectly, $V_m(g) = RT/p$

$$\frac{dp}{dT} = \frac{\Delta_{\text{vap}} H}{T (RT/p)}, \quad \frac{d \ln p}{dT} = \frac{\Delta_{\text{vap}} H}{RT^2}$$

since $dx/x = d \ln x$. If $\Delta_{\text{vap}} H$ is independent of temperature, then integration of this equation yields

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

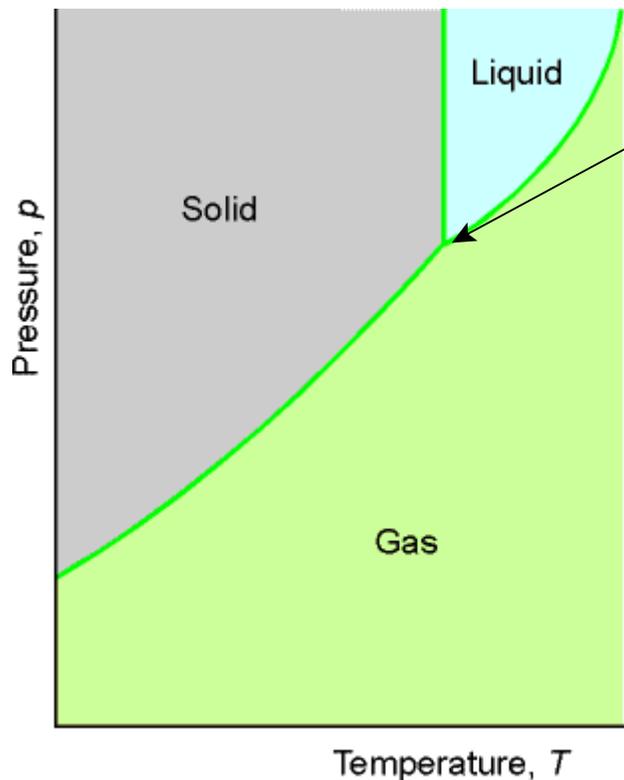
where p^* is the vapour pressure when temperature is T^* , and p for T (as shown in the plot) - this plot will not extend beyond T_c , since there is no liquid phase at that point



Solid-Vapour Boundary

This is treated exactly in the manner as the liquid-vapour boundary, replacing $\Delta_{\text{vap}}H$ with $\Delta_{\text{sub}}H$, the enthalpy of sublimation

Since $\Delta_{\text{vap}}H < \Delta_{\text{sub}}H$, the equation predicts a steeper slope for the sublimation curve than the vapourization curve at similar temperatures



Note the very similar slopes where the solid and liquid boundaries meet