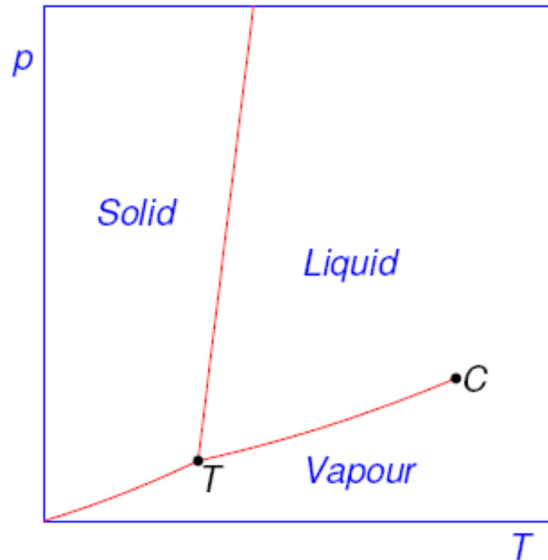# *Phase Transitions*

Chapter 4

Phase Transitions

4.1 Real Gases

4.2 Van der Waals' equation

4.3 Properties of van der Waals' equation

4.4 Liquefaction: example of use of real gas properties

4.5 Introduction to Phase Transitions

**4.6 Clausius-Clapeyron Equation**

4.7 Integration of CC-Equation

4.8 Examples

4.1 Real Gases

- **Ideal gas.** Assumed to have negligible molecular size and no long-range forces (i.e. only kinetic energy).

- The molecules of a real gas occupy real space and will hit the walls sooner and more often than if they were points-increasing the pressure significantly if n/V is high.

- The molecules of a real gas have long range attractions each – so tend to spend longer in each others vicinity at low temperatures and tend to 'pull back' molecules heading for the walls – reducing the no that are free to hit the walls, and the speed with which those that do hit arrive, so reducing the pressure.
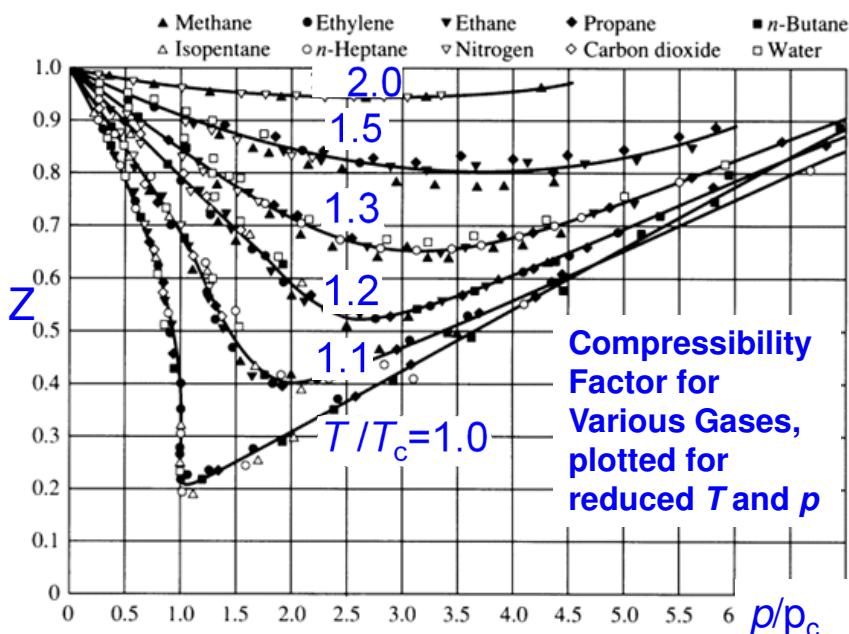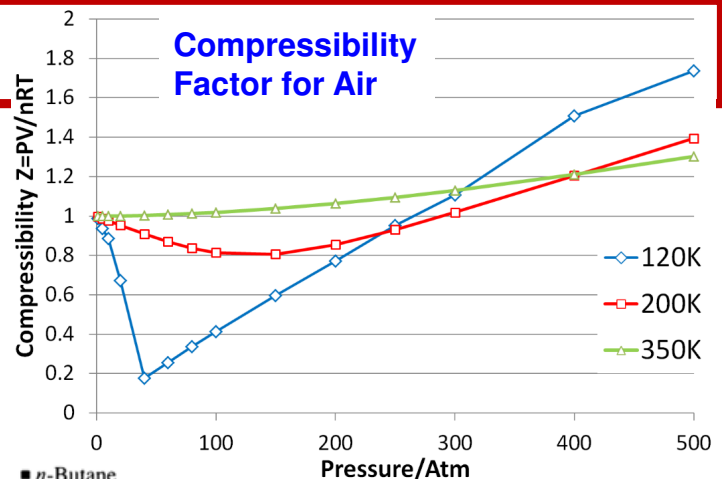
Large Molecules, hit wall/each other more often
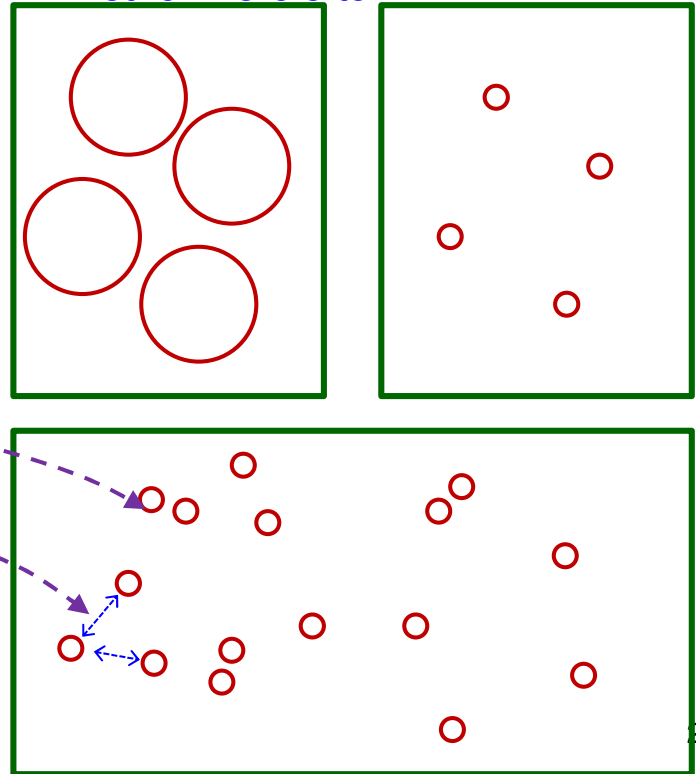
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Real Gases

- Convenient to plot **compressibility factor** $Z = \dfrac{pV}{nRT}$

Compressibility Z=PV/nRT

Compressibility Factor for Air

- ◇ 120K
- □ 200K
- △ 350K

Pressure/Atm

▲ Methane   ● Ethylene   ▼ Ethane   ◆ Propane   ■ n-Butane
△ Isopentane   ○ n-Heptane   ▽ Nitrogen   ◇ Carbon dioxide   □ Water

Z

2.0
1.5
1.3
1.2
1.1
$T/T_c=1.0$

Compressibility Factor for Various Gases, plotted for reduced T and p

p/p_c

Theorem of corresponding states: All fluids have approximately the same compressibility factor when the pressure and temperature are expressed in reduced units – *i.e.* as fractions of the fluid's critical temperature and pressure

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Boyle's Law Revisited

● How might you parameterise/model empirically this deviation from ideal behaviour: could take ideal behaviour in terms of Boyles law as a starting point:

> "If temperature is constant, then pV =constant."

● For a real gas, never strictly true. Can expand:
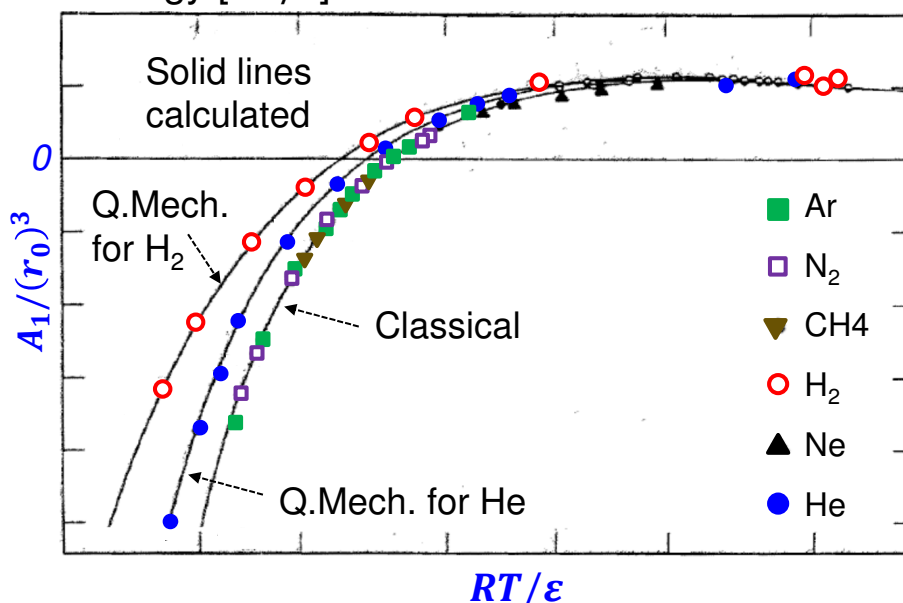
$$pV = A_0 + A_1 p + A_2 p^2 + A_3 p^3 + ...$$

Called a "*Virial expansion*". Could also expand in powers of 1/V.

● At sufficiently low p, Boyle's law will become an arbitrarily good approximation.

● Virial coefficients A_0, A_1, … will be functions of T.

● For a real gas, the Boyle temperature, T_B, is defined as the temperature at which $A_1 = 0$, i.e. at which Boyle's Law is most closely obeyed.

Boyle Temperature

● In order to compare the behaviour of different gases plot A_1 'reduced' by dividing by (molecule size)^3 [$A_1/(r_0)^3$] against RT/molar dimer binding energy [RT/ε].

Solid lines calculated

Q.Mech. for H_2

Classical

Q.Mech. for He

$A_1/(r_0)^3$

0

RT/ε

Legend:
- ■ Ar
- □ N_2
- ▼ CH4
- ○ H_2
- ▲ Ne
- ● He

● At the Boyle temperature the long-range attraction cancels exactly the short-range repulsion between 'real' molecules.

● An example of the law of corresponding states – *i.e.* gasses have the same properties if plotted in reduced variables.

● Corresponding states notion breaks down for H_2 and He because they are so light that the quantum mechanics of the interactions become important at low temperatures (long wavelengths)

[Data from R.J. Lunbeck, Ph.D thesis, Amsterdam 1950, Figure derived from J.O.Hirschfelder, C.F. Curtiss and R.B.Bird,'Molecular Theory of Gases and Liquids', Wiley, NY 1954]

4.2 Van der Waals' Equation

- **Ideal gas**. Assumptions of negligible molecular size and no long-range forces (i.e. only kinetic energy) led, through kinetic theory, to the ideal gas equation $pV = RT$.

- It would be useful to have an approximate parametrisation of the equation of state of a real gas to 'play with' and get a feel for how a real gas behaves. (If you have a real application, either look up the measured detailed properties, or use a parameterised fit to the compressibility factor if the full properties have not been measured for this gas.)

- Two important factors need to be taken into account:

  - ❋ Finite molecular size.
  - ❋ Intermolecular attraction.

- Several such equations exist. Best known is **van der Waals' equation.**
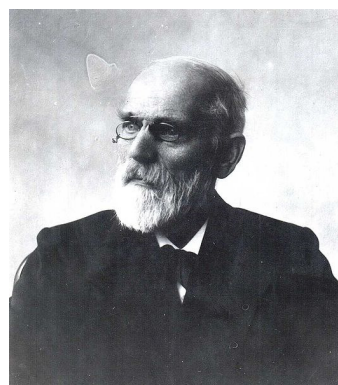
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Molecular Size

- The volume available to 1 mole of molecules is not the full V but $(V - b)$.

- Estimate b by simple hard sphere model; where the sphere radius = r.

  - ❋ Each molecule excludes a spherical volume $\frac{4}{3}\pi(2r)^3$ within which no other molecule can reside.

  - ❋ Hence, for one mole

$$b = \left(\frac{1}{2}\right) N_A \frac{4}{3} \pi (2r)^3 = N_A (16/3) \pi r^3$$

    2r

    The factor ½ arises because the key situation is when a collision occurs – so one considers how much space is 'off limits' for a PAIR of atoms
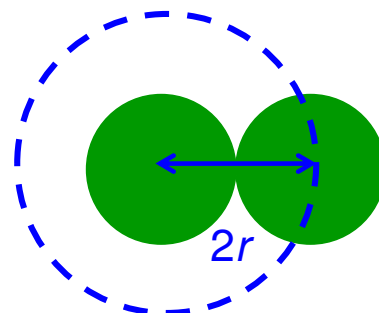
- In practice one would fit b to experimental data, but the above gives a reasonable estimate.

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Intermolecular Forces

- Molecules hitting walls are slowed down owing to attractive forces from molecules in the bulk of the gas.

- Hence the pressure at the walls is **slightly less** than in the bulk.

- Van der Waals takes this into account by replacing *p* by
$$\left(p + \frac{a}{V^2}\right)$$ in the ideal gas equation.

- Rational for this way of modelling the pressure reduction:
  - ✳ Rate of molecules hitting walls $\propto \rho$ (density)
  - ✳ Number of molecules pulling them back is also $\propto \rho$
  - ✳ Hence $\qquad \delta p \propto \rho^2 \propto \dfrac{1}{V^2}$

Van der Waals' Equation

- Therefore, we have a van der Waals' equation (for one mole)
$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

- Or for *n* moles:
$$\boxed{\left(p + n^2\frac{a}{V^2}\right)(V - nb) = nRT}$$

- *a* and *b* can be determined empirically by fitting real data.

Van der Waals' Isotherms

- At high T, $pV = RT$ is still a good approximation.

- **C** is a point of inflection, denoting the "Critical Temperature" T_C.

- For $T < T_C$, something rather complicated is going on.

- Real gases liquefy at high p and low T. This helps us to interpret what is going on...

*van der Waals isotherms*
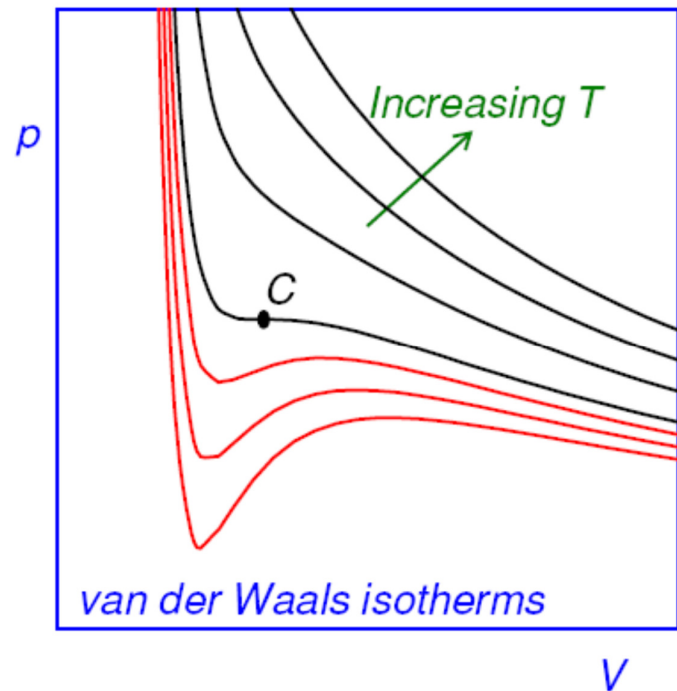
Van der Waals' Isotherms

- Consider a single isotherm below T_C; (real isotherm solid; van der Waals' dashed).

- $V > V_D \rightarrow$ **gas**

- $V < V_A \rightarrow$ **liquid**.

  V hardly changes; V is close to the value of b.

- A real gas proceeds at constant p from D $\rightarrow$ A as gas liquefies; **both phases coexist in equilibrium**.

- How do we decide where to draw line AB? Use 'Maxwell area rule: integral of area between dashed and solid lines is zero (same area above and below). Reason? Change in F between A and D gives max work that can be done $= \int p dV$. F is a state function so we should draw line AD such that the work done along this path is the same as that done on the van der Waals isotherm A-B-C-D.
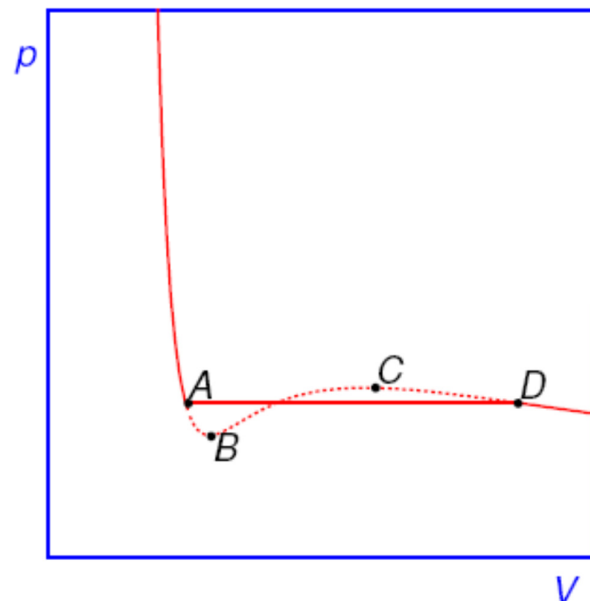
Liquid/gas Transition

- Nucleation (e.g. impurities) typically needed to induce phase changes. Very pure substances may be able to move along A → B (superheated liquid) or D → C (supercooled vapour).

- The region B → C is unphysical/unstable. Increase $V \Rightarrow$ increase p ; moves even more towards C.

- The critical temperature T_c is the highest temperature at which liquid and vapour can coexist. Critical point is (p_c, V_c, T_c)

van der Waals isotherms
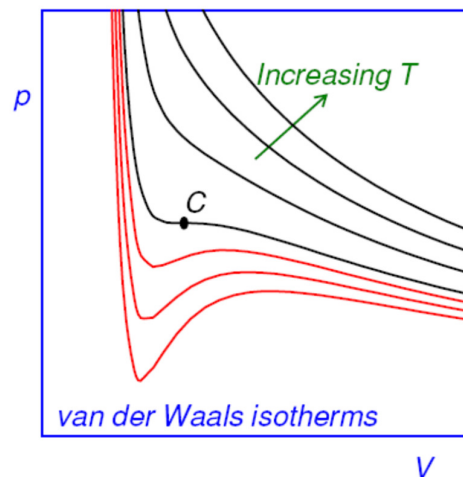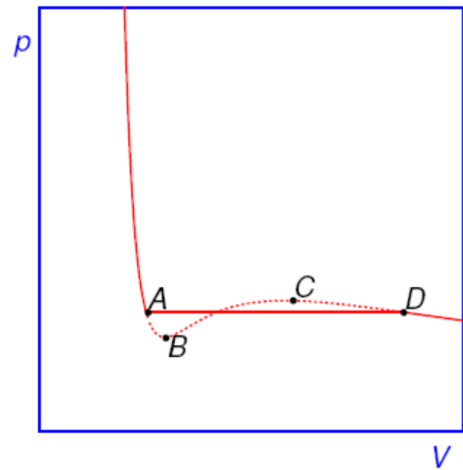
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Schematic PV Curves for Liquid/gas Transition

Critical T,V,P

Liquid expands as T rises
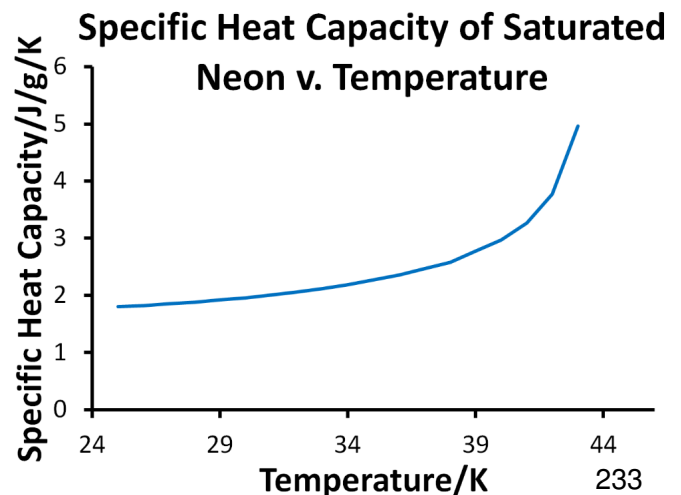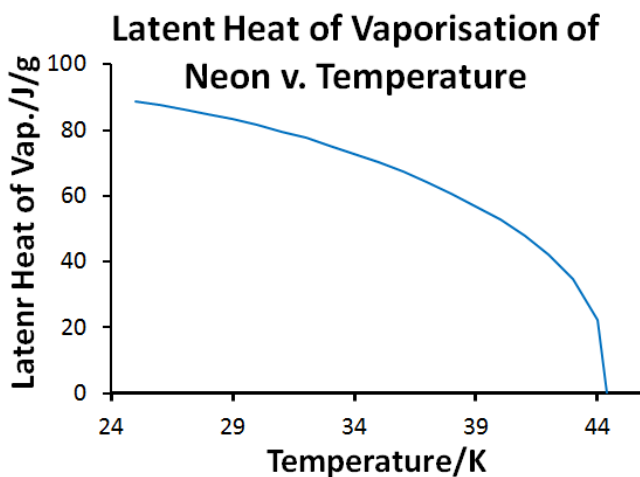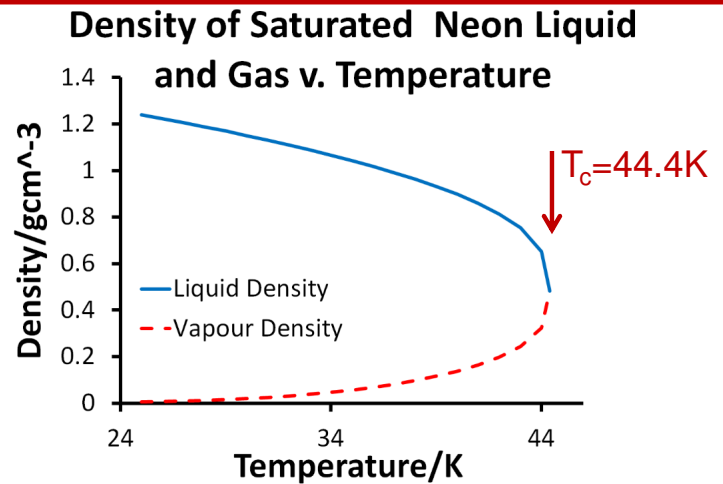
Increasing T
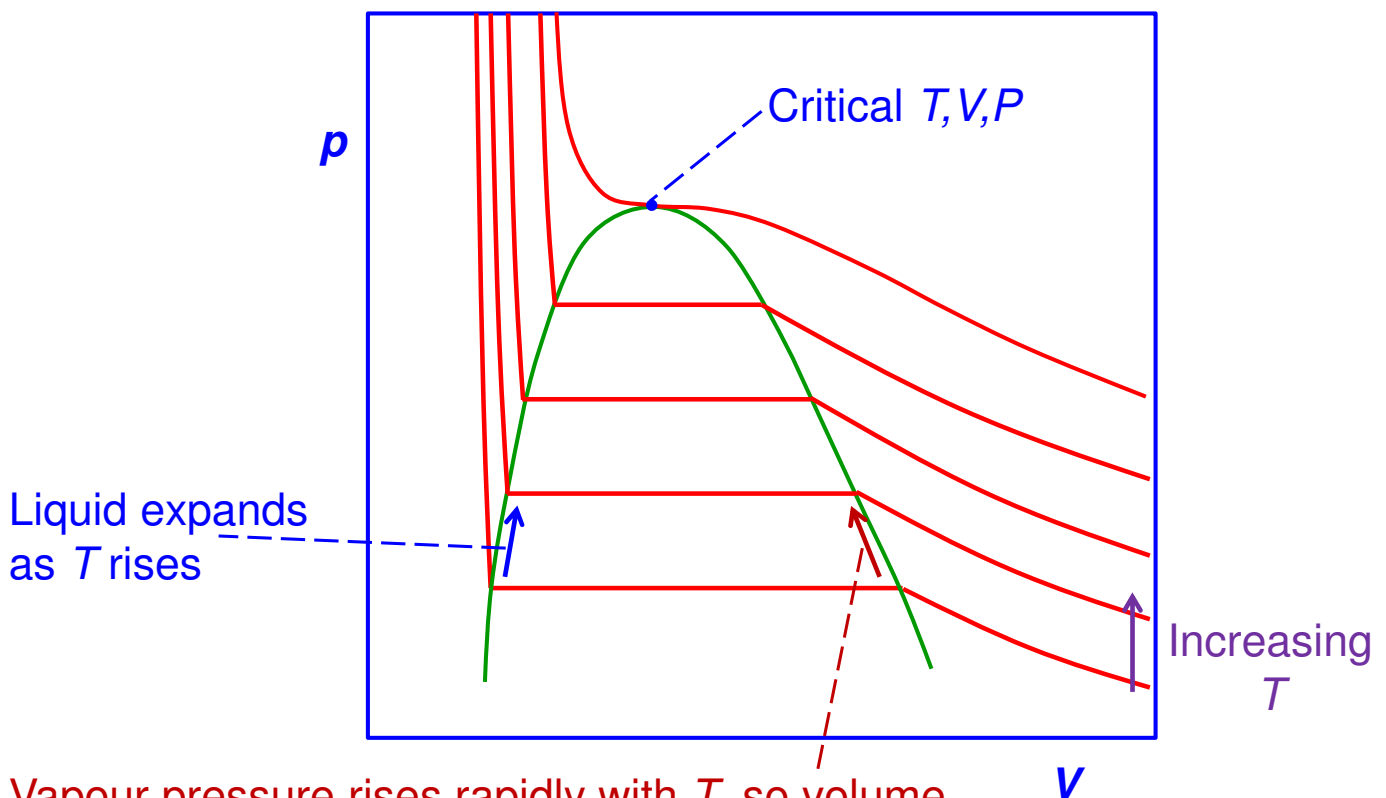
Vapour pressure rises rapidly with T, so volume at end of co-existence line drops as T rises

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What Happens at the Critical Temperature?

As T -> T_c liquid density starts to drop rapidly – and heat capacity rises (atoms moving apart, and energy needed to overcome attractive P.E.). At the same time the Vapour Density increases and the gas molecules feel the interaction potential, reducing the enthalpy of the gas. The Latent heat collapses, and gas density rises till the two phases become indistinguishable.

Density of Saturated Neon Liquid and Gas v. Temperature

T_c=44.4K

- Liquid Density
- Vapour Density

Latent Heat of Vaporisation of Neon v. Temperature

Specific Heat Capacity of Saturated Neon v. Temperature

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4.3 Properties of the vdW Equation

- Critical point = point of inflection

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$$

- Rearranging van der Waals' equation:

$$p = \frac{RT}{(V-b)} - \frac{a}{V^2}$$

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} = 0$$

- Eliminating $T \Rightarrow$ $\boxed{V_C = 3b}$

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Properties of the vdW Equation

- Substitute back to get T_C and p_C:

$$V_C = 3b \qquad T_C = \frac{8a}{27Rb} \qquad p_C = \frac{a}{27b^2}$$

- Compressibility factor at critical point: $\quad Z_c = \dfrac{p_c V_c}{n T_c} = \dfrac{3}{8}$

Gas	H_2O	He	H_2	Ne	N_2	Ar
Z_c	0.23	0.30	0.30	0.29	0.29	0.29

- Boyle temperature? Virial expansion in $1/V$:

$$pV = \frac{RTV}{(V-b)} - \frac{a}{V^2} \cdot V = RT\left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{V}$$

$$= RT + \underbrace{\frac{1}{V}(RTb - a)}_{\textbf{= 0 at } T_b} + \mathcal{O}\left(\frac{1}{V^2}\right)$$

- Hence $T_b = a/Rb$
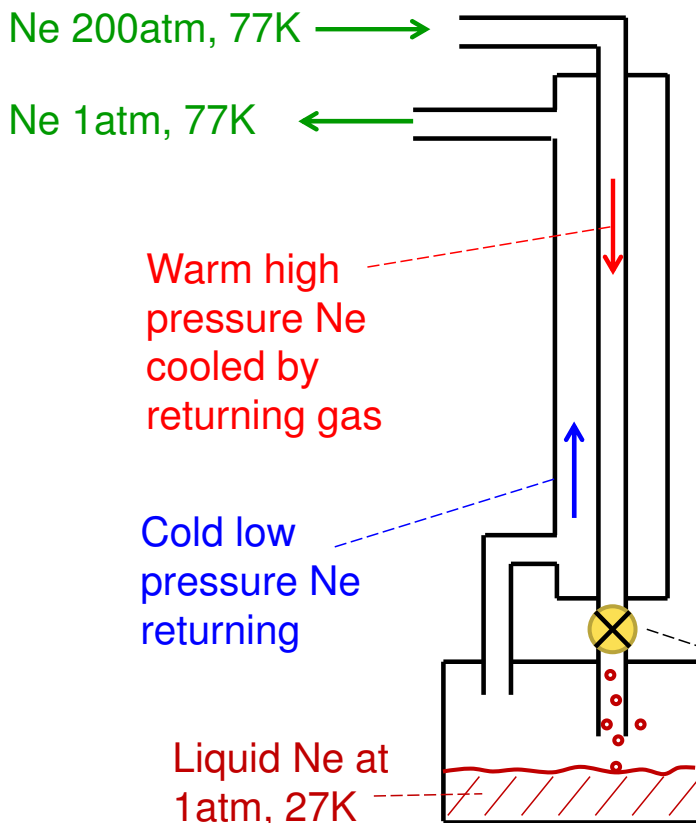
4.4 Liquefaction of Gases

- The most efficient way of cooling a gas is via adiabatic expansion, but this requires a heat engine (moving, lubricated piston) working at very low temperatures. One can liquify a gas just by expanding it through a partially open 'throttling' valve which maintains a pressure difference across it.
- Remember for a flow process with no energy input, H is conserved.
- If a real gas is expanded through a valve its temperature will change. At low temperatures and modest to low pressures the attractive forces dominate and the gas cools, whereas above a certain temperature (the 'inversion temperature' where weak attractive forces become not so important) and high pressure, the short range repulsive forces dominate and the gas warms up.
- Rate of temperature change given by Joule-Thomson coefficient: $\qquad \mu_{JT} = \left(\dfrac{\partial T}{\partial P}\right)_H$
- The basic trick in gas liquefaction is to expand a gas from high pressure below the inversion temperature – all you need is a heat exchanger and a throttling valve, but often several stages.

Gas	O_2	N_2	Ne	H_2	He
Inversion T at 1atm/K	764	621	250	202	51

Liquefaction of Gases: an Example

● Remember for a flow process with no energy input, *H* is conserved

(In this example we are assuming the Ne is precooled by liquid nitrogen at 77K)

Ne 200atm, 77K ⟶

Ne 1atm, 77K ⟵

Warm high pressure Ne cooled by returning gas

Cold low pressure Ne returning

Liquid Ne at 1atm, 27K

'Joule-Thomson' expansion valve

Specific *H* Ne@ 200atm, 77K =108J/g

Specific *H* Ne@ 1atm, 77K =144J/g

Specific *H* Ne liquid @ 1atm, 27K =5J/g

Conserving *H*, if for every gram of Ne supplied, *x* gram liquefies:
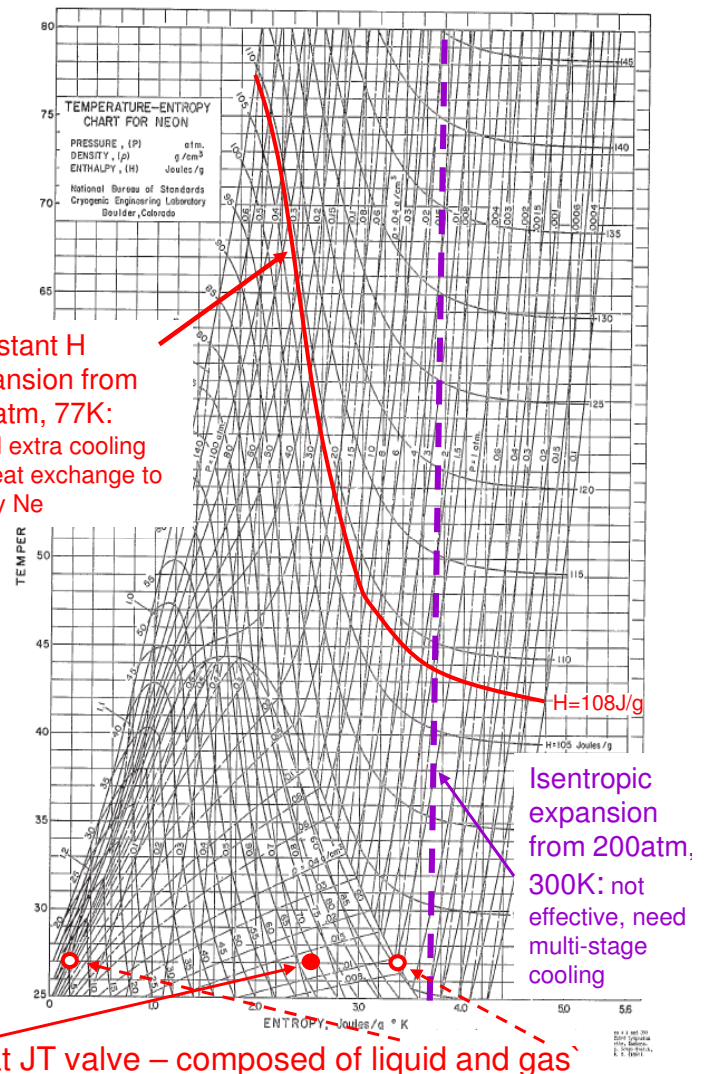
$$108 = 144(1-x) + 5x$$
$$x = 0.26$$

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Isobars/atm

TEMPERATURE–ENTROPY CHART FOR NEON

PRESSURE , (P)   atm.
DENSITY , (ρ)   g/cm³
ENTHALPY , (H)   Joules/g

National Bureau of Standards
Cryogenic Engineering Laboratory
Boulder, Colorado

H=100J/g

H=250J/g

H=200J/g

H=150J/g

H=100J/g

TEMPERATURE , °K

Constant density lines

ENTROPY, Joules/g °K

V–F–2

TEMPERATURE–ENTROPY CHART FOR NEON

PRESSURE , (P)   atm.
DENSITY , (ρ)   g/cm³
ENTHALPY , (H)   Joules/g

National Bureau of Standards
Cryogenic Engineering Laboratory
Boulder, Colorado

Constant H expansion from 200atm, 77K: Need extra cooling by heat exchange to liquify Ne

H=108J/g

Isentropic expansion from 200atm, 300K: not effective, need multi-stage cooling

TEMPER

ENTROPY, Joules/g °K

H for Ne at JT valve – composed of liquid and gas`

4.5 Introduction to Phase Transitions

- In discussing van der Waals' equation, we encountered the idea of a phase transition gas ↔ liquid.

- On a molecular level, it is possible for a molecule in a liquid close to the surface to have sufficient energy to escape the intermolecular forces of its neighbours, and enter the gas phase.

- Equally, if there is vapour above the liquid surface, gas molecules may hit the surface and stick.

- At any given temperature there will be some pressure at which these two processes are in dynamic balance in a closed system. This is the vapour pressure.

Vapor

Liquid

- This is an example of a very general phenomenon of co-existence of two phases with a flux of particles between the 239 two phases.
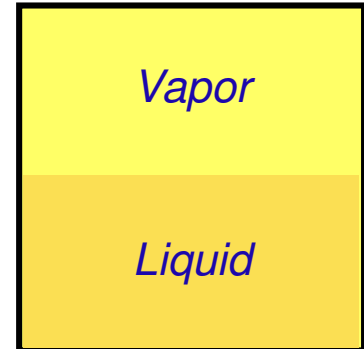
# Phases of Matter

- Substances usually exist in (at least) three phases:
    - Gas – molecular spacing >> size;
      random diffusive motion.
    - Liquid – molecular spacing ~ size;
      random diffusive motion.
    - Solid – molecular spacing ~ size;
      atoms vibrate about mean positions

- There may be several solid phases (polymorphism).

- Thermodynamics can make general statements about **phase changes**.

- We shall show in the Stat. Thermo. section later that, provided the temperature is high enough for quantum effects not to be important, the mean KE of atoms/ c.o.m of molecules is the same in all phases.
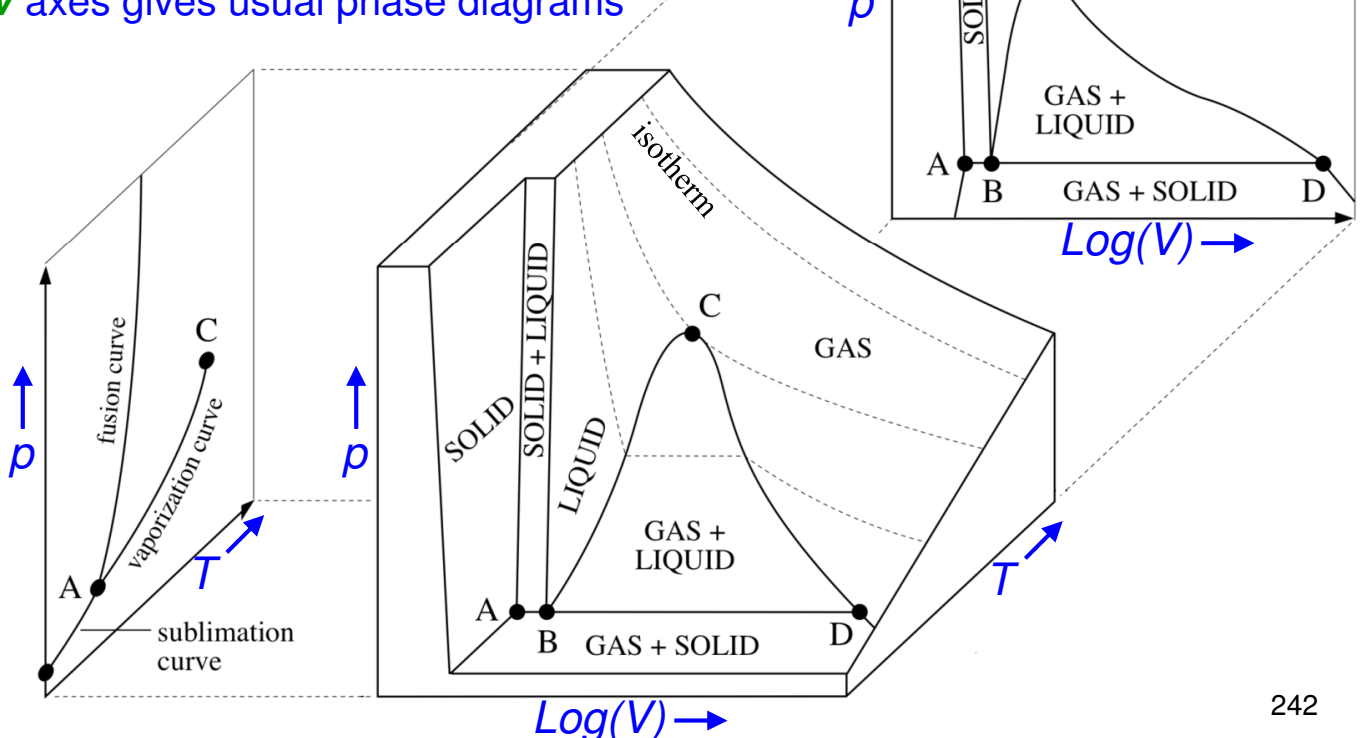
Phase Diagram

- Usually represented on a $p - T$ phase diagram.

- A single component system its defined by three variables – originally volume, energy and contents (V, U, N) – but can also be given by e.g. p, N and T. If you plot a 2D diagram – tacitly assuming one variable is fixed, or does not affect the diagram – for a p-T (both intensive) this is the amount of material. This leaves 2 free variables – you can be anywhere in the diagram – but if you add a constraint (e.g. solid and liquid must coexist) this limits you to being on a line.

- Lines represent values of these intensive variables at which pairs of phases coexist.

- Otherwise only one phase is stable.

- **T** is the Triple point at which all three phases coexist.

- **C** = critical point, above which gas and liquid are not distinguishable.

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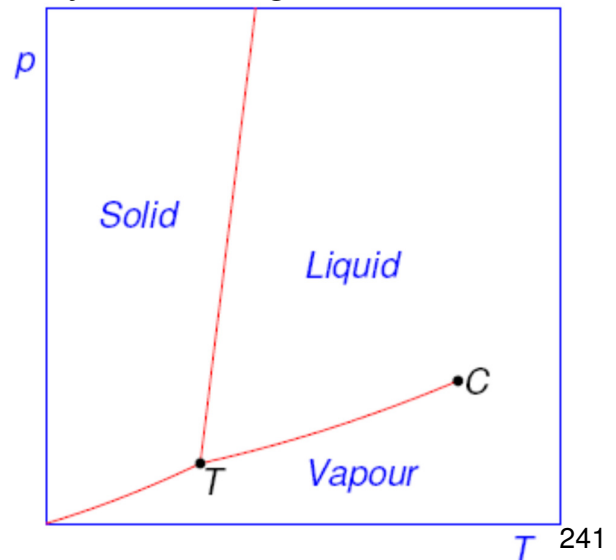
Typical P-V-T diagram

- Plot a surface made up of **p** v. **V** lines at a series of temperatures for a typical material that expands on melting
- Projections of boundaries onto **p**/**T** and **p**/**V** axes gives usual phase diagrams


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Phase Diagram - Water

- Lines generally have positive slope – volume generally increases as you go thorough a phase transition by increasing the temperature and Le Chatelier's principle indicates that as you increase the pressure, the system will react to reduce its volume, so will tend to go to the more dense phase, and you need a higher temperature for it to melt. Solid-liquid slope usually very steep.

- But there is a negative slope for the solid-liquid equilibrium for **H₂O** (due to expansion of water on freezing- explained later.)

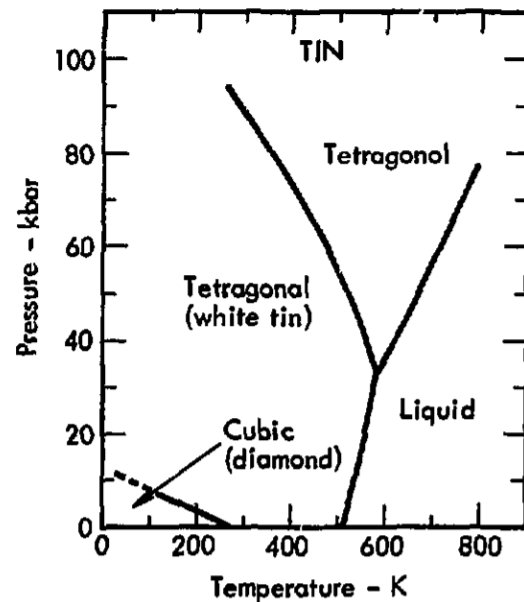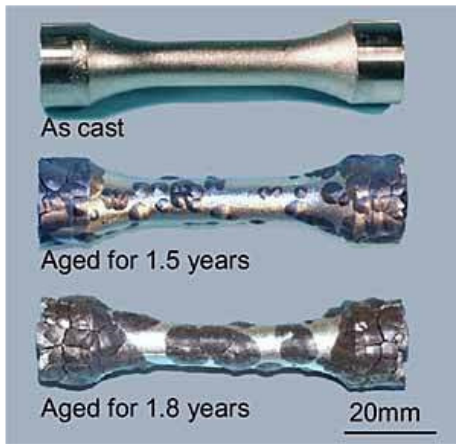- Triple point for water lies 0.01 K above the freezing point at 1 atm.
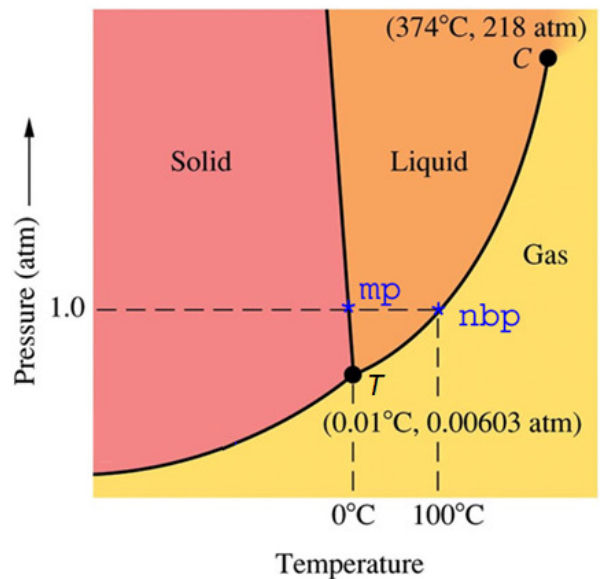
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Phase Diagram - Water

http://ergodic.ugr.es/termo/lecciones/water1.html

244
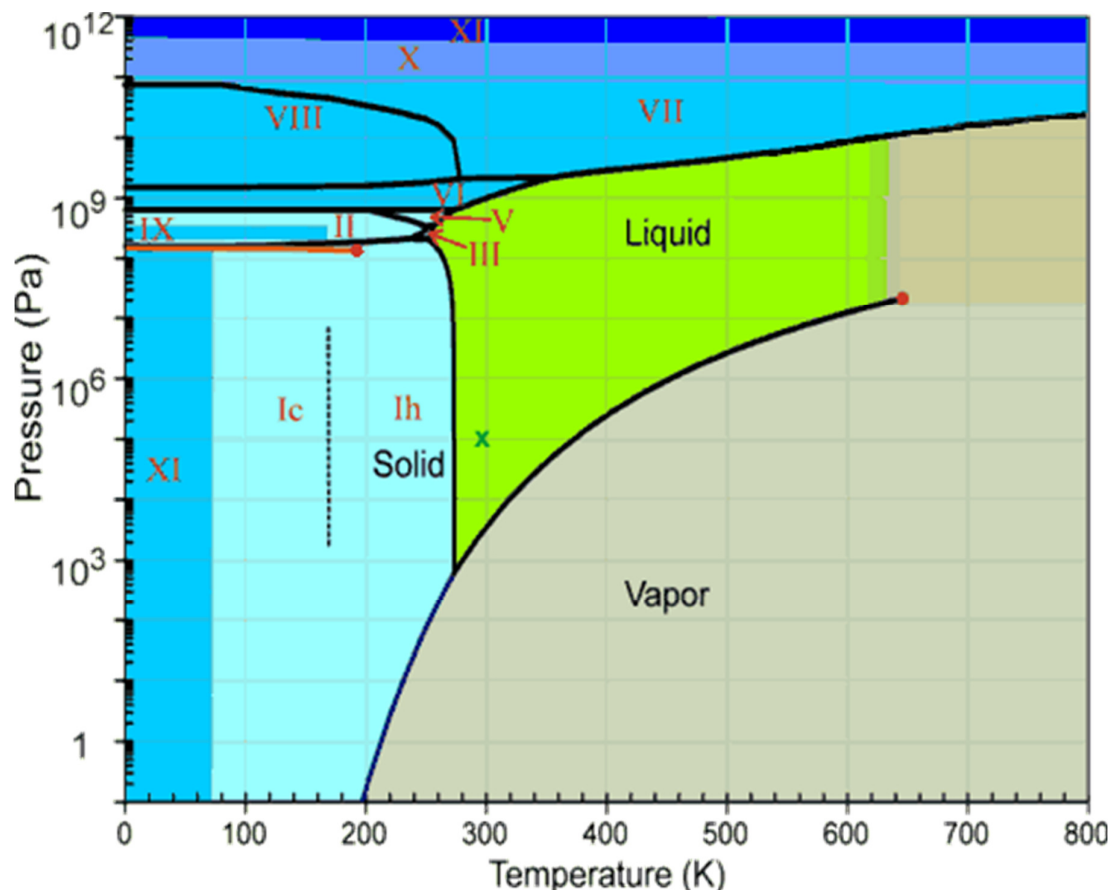
Tin has two allotropic forms. "Normal" or white *beta tin* has a stable tetragonal crystal structure and is a metal. Below about $T = 13.2°$ C, beta tin turns extremely slowly into *alpha tin*. "Grey" or alpha tin has a cubic, diamond structure (cf Silicon as well) and is also a semiconductor, not a metal. The expansion of tin from white to grey causes most tin objects to crumble.

Phase Transition

General features:

- Entropy change (change of order) $\Rightarrow$ transfer of heat from surroundings needed if $S_{universe}$ to remain constant. Latent heat $L = T\Delta S$.

- Volume change.

- Note: strictly these remarks refer to **first order** phase transitions.

- There exist **2nd** - and **higher-order** phase changes.

  Example: in 2nd-order, there is discontinuity in heat capacity

$$T\left(\frac{\partial S}{\partial T}\right)$$ rather than in entropy S.

4.6 Clausius-Clapeyron Equation
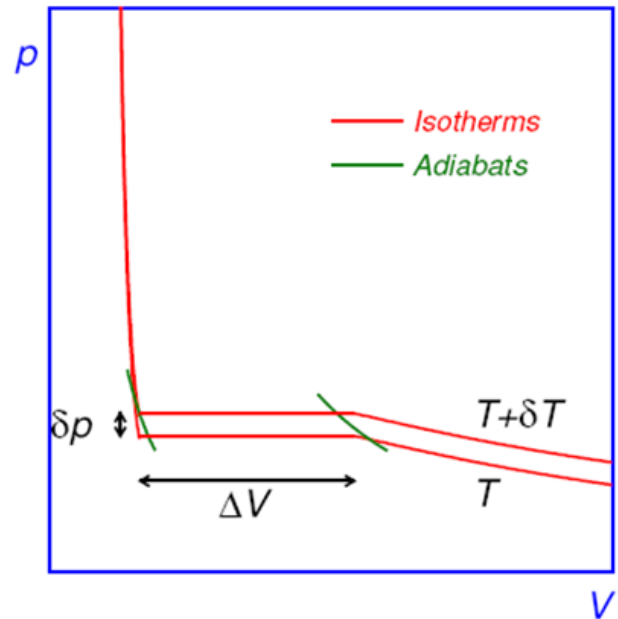
- Want to compute phase equilibrium curve in *p-T* plane.

- Start with liquid-gas case.

- Consider two isotherms *T* and *T + δT* on *p-V* diagram.

- Connect them with two adiabatics as shown.

- This forms a Carnot cycle with efficiency:

$$\eta = \frac{W}{Q} = \frac{\delta T}{T}$$

Clausius-Clapeyron Equation
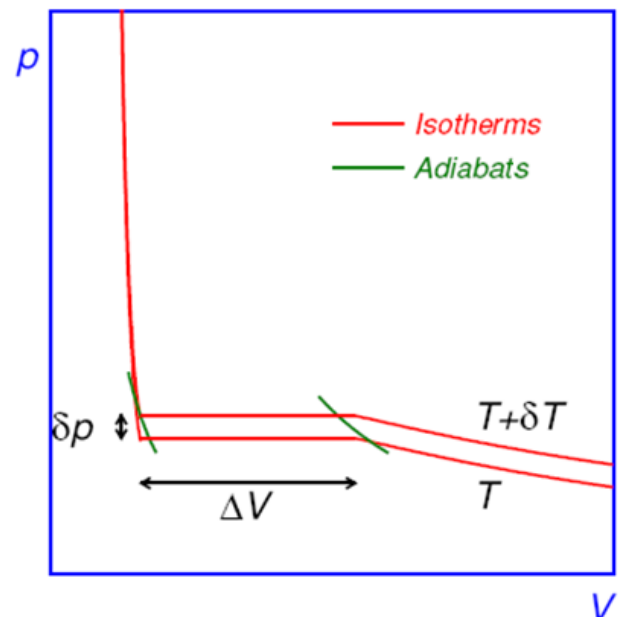
- *Q* is latent heat: $Q = L = T\Delta S$

- *W* is work done = area of cycle
$$= \delta p \Delta V$$

$$\Rightarrow \quad \frac{\delta T}{T} = \frac{\delta p}{T}\frac{\Delta V}{\Delta S}$$

- Take limit as δT → 0:

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V}$$

- This is the Clausius-Clapeyron equation.
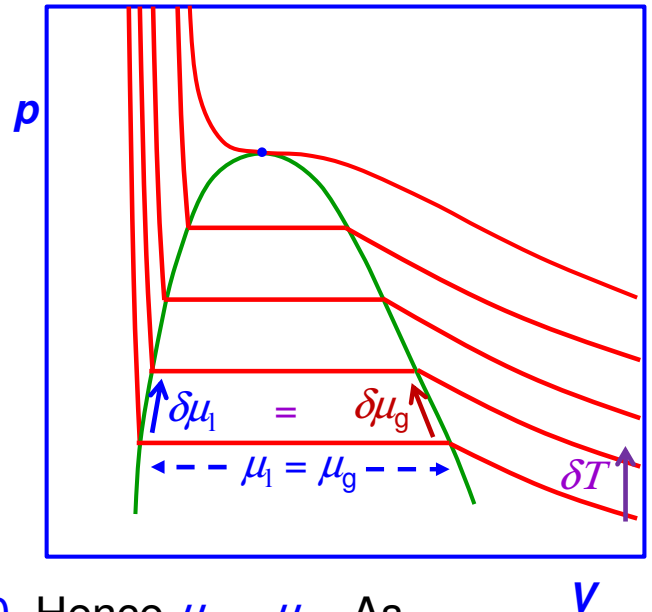
Alternative Derivation of C.C. Equation

- When discussing thermodynamic potentials, we argued that Gibbs free energy should be minimised in a system at fixed T, p.

- Suppose we have two phases, particle numbers N_1, N_2 in each (with $N_1 + N_2$ = const.). Chemical potential (Gibbs free energy per particle) μ_1 and μ_2 respectively, then we have:

$$G = N_1\mu_1 + N_2\mu_2$$
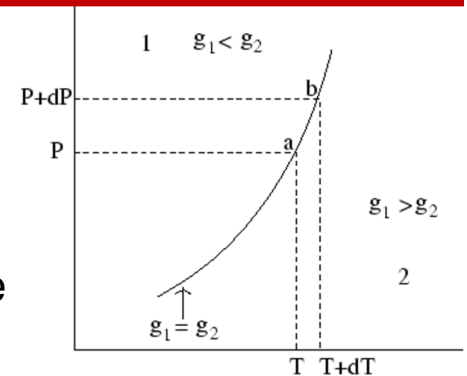
- At equilibrium:

$$dG = 0 = dN_1\mu_1 + dN_2\mu_2$$

- But, $N_1 + N_2$ = const. $\Rightarrow$ $dN_1 + dN_2 = 0$. Hence $\mu_1 = \mu_2$. As previously shown, the chemical potentials for the two phases are equal and as you go along the phase boundaries for a particular change in temperature, $\delta\mu_1 = \delta\mu_2$.

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Alternative Derivation ...

- Consider two points *a* and *b* on the phase boundary. At each, $\mu_1 = \mu_2$. Hence $\delta\mu$ going between *A* and *B* is the same for each phase. To make the maths easier to 'recognise' – work with 1 mole of substance – so $G = \mu$:

$$\underbrace{\left(\frac{\partial G_1}{\partial T}\right)_p \delta T + \left(\frac{\partial G_1}{\partial p}\right)_T \delta p}_{\delta G_1} = \underbrace{\left(\frac{\partial G_2}{\partial T}\right)_p \delta T + \left(\frac{\partial G_2}{\partial p}\right)_T \delta p}_{\delta G_2}$$

- But $dG = -SdT + Vdp$, $\Rightarrow$ $\left(\frac{\partial G}{\partial T}\right)_p = -S$ and $\left(\frac{\partial G}{\partial p}\right)_T = V$

- Hence:

$$(S_2 - S_1)\delta T = (V_2 - V_1)\delta p \quad \Rightarrow \quad \frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V} \quad \text{as before.}$$

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4.7 Integration of Clausius-Clapeyron Equation

- Other forms of Clausius-Clapeyron equation are possible, under various simplifying assumptions.

- Vapour is typically ~ 1000 × less dense than liquid (or solid). So for liquid-vapour (or solid-vapour) transitions, $\Delta V \approx V_{\text{vap.}}$.

- And if the pressure is sufficiently low (and far from critical point), the vapour may be approximated by the ideal gas equation,
$$\Delta V \simeq RT/p$$

… in which case:
$$\frac{dp}{dT} \simeq \frac{Lp}{RT^2}$$

Integration of Clausius-Clapeyron Equation

$$\frac{dp}{dT} \simeq \frac{Lp}{RT^2}$$

- To go further, we need to know the temperature dependence of latent heat L.

- For small enough temperature intervals, we may be able to approximate $L \simeq$ const.
$$\int \frac{dp}{p} = \frac{L}{R} \int \frac{dT}{T^2} \quad \Rightarrow \quad \ln p = \frac{L}{RT} + \text{const.}$$
$$\Rightarrow \quad p = p_0 e^{-L/RT}$$

- Suggestive of Boltzmann factor; probability of molecule having enough energy to escape.

4.8 Examples

- Boiling point of water: it boils at the temperature where vapour pressure = ambient atmospheric pressure.

- For H_2O latent heat L = 2 MJ kg^{-1} = 36 kJ mol^{-1}.

- Atmospheric pressure falls with height: $p = p_0 e^{-mgh/kT}$ (for isothermal atmosphere).

- Estimate boiling point of water on top of Everest? $h \sim 8000m \Rightarrow$ $p/p_0 \sim 0.40$, or $\delta p/p_0 \sim -0.60$

- Clausius-Claperyron $\Rightarrow$ $\quad \delta T \approx \dfrac{\delta p}{p} \cdot \dfrac{RT^2}{L} \approx -10K$

- Actually, an isothermal atmosphere is not a very good model –the temperature drops with altitude due mainly to adiabatic cooling as air rises and expands. The International Standard Atmosphere (ISA) has a lapse rate of 6.5 K/km in the Troposphere (up to 11km). The dry air adiabatic lapse rate is 9.8 K/km and the moist (ie condensation occurring) rate is typically 5 K/km. For Everest p/p_0= 0.33)

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Freezing of Water

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V}$$

- Liquid → Solid. For most substances $\Delta S < 0$ (Heat transferred out of material as it freezes) and $\Delta V < 0$ (solid is more dense than the liquid). $\Rightarrow dp/dT > 0$.

- Also, ΔV usually quite small, hence $dp/dT = \Delta S/\Delta V$ is steep.

- Water is unusual as $\Delta V > 0$: water expands on freezing (burst pipes etc.) $\Rightarrow$ $dp/dT < 0$.

Water Phase Diagram

- Increasing pressure reduces the freezing point. It has been proposed that the pressure under a skate melts the ice and provides lubrication – but this melting point reduction is modest – maybe 3.5C, and in any case snow is slippery to skis. The answer seems to be that ice 'pre-melts' – has a thin layer of water on its surface. This was proposed by Faraday and justified by Gibbs, and explains why if you put ice on ice it sticks (hence snow balls – does not work with sand…)
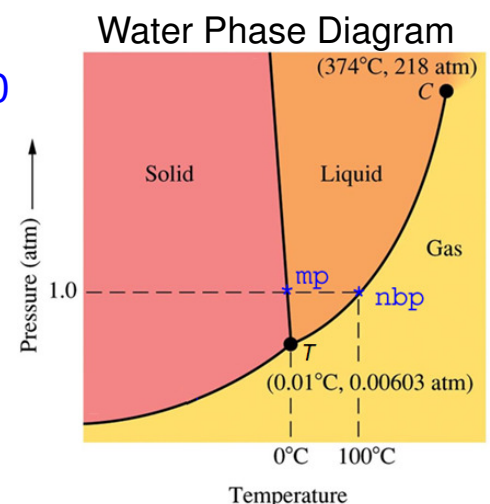
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Chapter 4: Summary

- Real gases: finite molecular size and intermolecular forces.

- Use of compressibility factor ($Z = \frac{pV}{nRT}$) , theorem of corresponding states.

- van der Waals' equation (for 1 mole) $\left(p + \dfrac{a}{V^2} \right) (V - b) = RT$

- Behaviour as critical temperature is approached: the liquid starts to expand rapidly against anharmonic particle-particle PE, and meets the number density and PE of an every higher density gas phase, latent heat collapses

- Equilibrium curves in *p -V - T* space. Triple point and critical point.

- Form of equilibrium curve - Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T \Delta V}$$