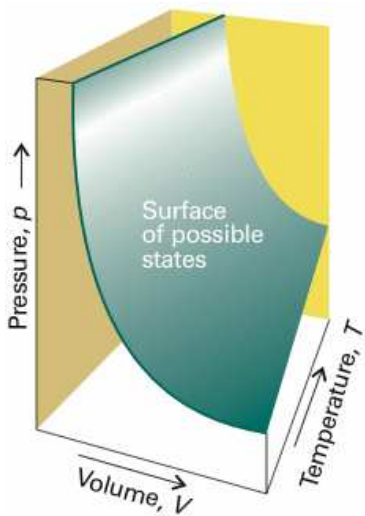


PREVIOUSLY ON

...*Thermodynamics*

- Black body radiation as Thermodynamics
- Stefan's T^4 Law
- $G=0$ for cavity radiation
- Planck's Energy distribution
- Existence proof of quantum mechanics

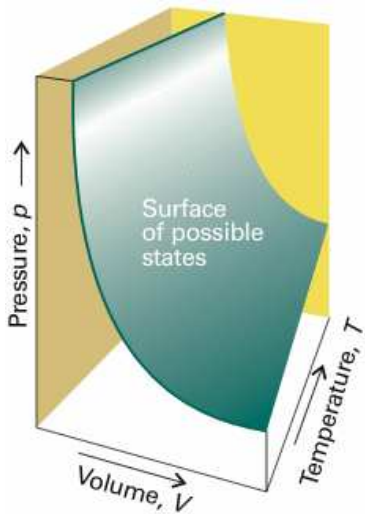
Ideal Gas Phase diagram



- A surface in 3D P, V, T space
- Given any two state variables, EoS gives third.

Phase diagram, (P, T) , (V, T) would be ...

Ideal Gas Phase diagram



- A surface in 3D P, V, T space
- Given any two state variables, EoS gives third.

Phase diagram, (P, T) , (V, T) would be ...
a square with "Gas" written on it.

Ideal Gas Energy

$PV = nRT$ doesn't tell us the energy (or H, F, G).

- Classical KE: $\frac{k_B T}{2}$ for each DoF
- Monatomic gas has 3 DoF: $u = \frac{3RT}{2}$
- Diatomic gas has 5 DoF: $u = \frac{5RT}{2}$

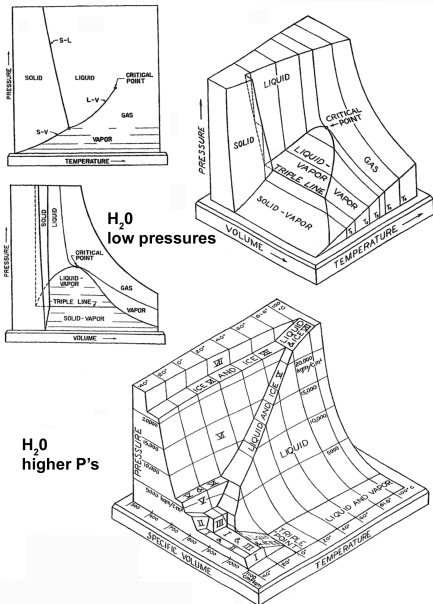
Real gas, depends on temperature and quantum rotors/vibrations

Recall $N_A k_B = R$

Real Phase diagrams

- Are not analytic functions.
- Are not continuous functions
- Are not differentiable (at phase transitions)

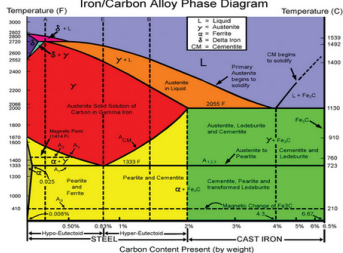
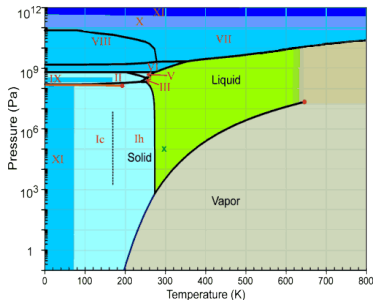
Water Equation of state



Equation of state for water

- A surface in 3D P,V,T space
- Given any two state variables, EoS gives third.
- Isenthalps, isentropes etc are lines on the surface.
- Lines separate phase(s).
- Magnetic phases may extend to a surface in higher dimension.

Water and Steel Phase Diagrams - Different axes



- A 2D graph labelling which phases exist
Lines are Phase Boundaries: Boiling, melting etc.
- Magnetic phases may extend phase diagram to higher dimension.
- More than one component - composition axis
Melting, Solubility limits, two phases
- Stable phase has lowest Free Energy

From Equation of state to Phase diagram

- Equation of state : Plane in space on thermodynamic coordinates.
- Each Phase: Smooth Plane in space.
- Between Phases: EoS is discontinuous
- Stable Phase
Lowest $G=U-TS+PV$
High T favours high entropy phases.
High P favours high density phases.
- Continuation of EoS beyond transition: Metastable Phase
- Phase Diagram: 2D projection of EoS

Notes on Equilibrium and Phase diagrams:

- **Equilibrium condition**

Minimise free energy appropriate to boundary condition.

$F(V,T)$ allows phase coexistence, $G(P,T)$ does not.

- **Conjugate variables**

P,V are conjugate (appear together in free energy expressions).

If $\partial P/\partial V > 0$ free energy can be reduced by volume collapse.

Negative bulk modulus or heat capacity are not allowed.

- **Triple point**

Ice, water and water vapour coexist at a unique T and P .

- **Sublimation Line**

Solid-to-vapour transition, e.g “dry ice”, (solid CO_2)

- **Critical point**

Unique T,P point where dense gas is indistinguishable from liquid.

- **Phase transition Line**

Entropy, Volume are discontinuous here.

- **“Controlled” processes**

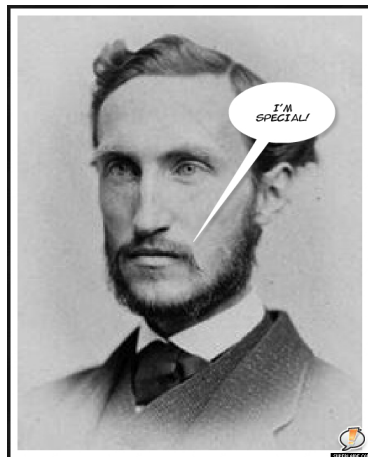
Iso- X -ic process is a line on the phase surface.

System in equilibrium with itself: Gibbs Free Energy

Two parts of a **System** in equilibrium:
constant T and P throughout
Mechanical (P) and Thermal (T) equilibrium
Relevant potential is Gibbs.

$$dG = VdP - SdT$$

System in mechanical and thermal
equilibrium minimises its Gibbs free energy.
Irreversible processes have $dG < 0$



Thermodynamically Impossible Properties

Negative Bulk Modulus: $K_S = -V \left(\frac{\partial P}{\partial V} \right)_S$

System with constant S , V boundaries. Two parts, A&B.

A grows by ΔV , so B shrinks by ΔV ;

$$\Delta U_A = \left(\frac{\partial U}{\partial V} \right)_S \Delta V + \left(\frac{\partial^2 U}{\partial V^2} \right)_S \frac{(\Delta V)^2}{2} + O(V^3)$$

$$\Delta U_B = - \left(\frac{\partial U}{\partial V} \right)_S \Delta V + \left(\frac{\partial^2 U}{\partial V^2} \right)_S \frac{(\Delta V)^2}{2} - O(V^3)$$

$$\Delta U = \Delta U_B + \Delta U_A = \left(\frac{\partial^2 U}{\partial V^2} \right)_S (\Delta V)^2 = -V \left(\frac{\partial P}{\partial V} \right)_S \frac{(\Delta V)^2}{V}$$

Using $\left(\frac{\partial U}{\partial V} \right)_S = -P$ from central equation $dU = TdS - PdV$.

Second Law: U is minimised at eq'm, so

$dU > 0$, V and $(\Delta V)^2$ are positive. So

$K_S = V \Delta U / \Delta V^2 > 0$, the adiabatic bulk modulus is positive.

Negative Specific Heat

Same argument for entropy at constant volume, dS .

$$dU = dU_B + dU_A = \left(\frac{\partial^2 U}{\partial S^2} \right)_v (\Delta S)^2 = \frac{1}{T} \left(\frac{\partial T}{\partial S} \right)_v T (\Delta S)^2 = \frac{T (\Delta S)^2}{c_v}$$

Positive dU , T and $(\Delta S)^2$ leads to $c_v > 0$.

The equilibrium condition for coexisting phases

Consider two coexisting phases

$$G = g_1 M_1 + g_2 M_2.$$

Mass conserved $dM_1 = -dM_2$.

Minimise G at equilibrium. $dG = g_1 dM_1 + g_2 dM_2 = 0$



Requires: $g_1 = g_2$

Specific Gibbs free energies are equal for coexisting phases

If $g_1 > g_2$, Second law allows transfer of material from 1 \rightarrow 2.

Three variables (P,V,T), two constraints (EoS and $g_1 = g_2$)

Phase coexistence is a line in P,T.

The Helmholtz function: equilibrium in fixed volume

Equilibrium for *system* at constant T , V :
minimise $F = U - TS$.

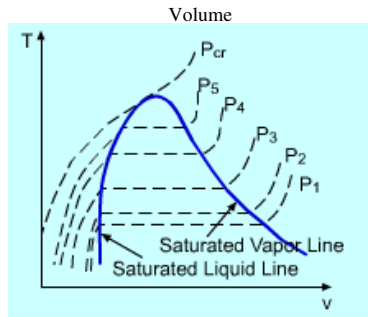
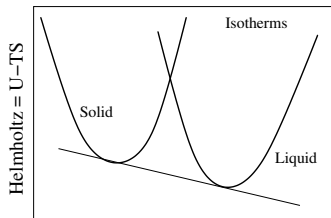
$$dF = PdV - SdT = 0$$

Subject to constraint:

$$V = v_1 M_1 + v_2 M_2$$

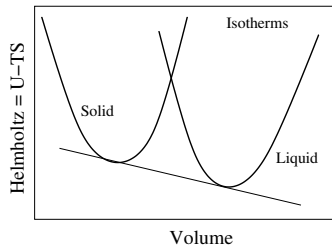
F minimised by a mixture of phases
The slope of common tangent is the
coexistence pressure

$$\left(\frac{\partial F}{\partial V}\right)_T = P$$



The Helmholtz function: equilibrium in fixed volume

Coexisting phases 1&2: $g_1 = g_2$
Different specific Helmholtz: $f_1 \neq f_2$



Different densities, $v_1 \neq v_2$

Total volume: $V = N_1 v_1 + N_2 v_2$ (lever rule).

Compression happens as material transforms into denser phase,
Isothermal ($dT = 0$) compressibility while phases coexist ($dG = 0$).

$$dP = (dG + SdT)/V = 0$$

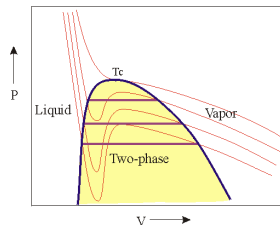
Material can compress with no change in pressure. Infinite compressibility!

Van der Waals fluid

Van der Waals EoS can be written:

$$Pv^3 - (Pb + RT)v^2 + av - ab = 0$$

- Cubic - $v(P, T)$ multivalued
- “Critical Point”: three roots coincide.
- For $T > T_c$, only one possible $v(P, T)$



Exercise: show vdW Critical Point $V_c = 3b$, $P_c = \frac{a}{27b^2}$, and $T_c = \frac{8a}{27Rb}$

Van der Waals equation in terms of critical point parameters

$$\left(P/P_c + \frac{3}{(V/V_c)^2} \right) \left(3 \frac{V}{V_c} - 1 \right) = 8 \frac{T}{T_c} \quad \text{VdW's Eqn of state}$$

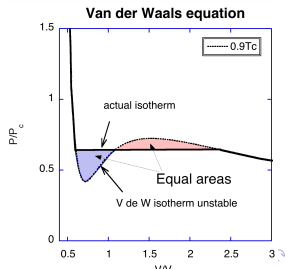
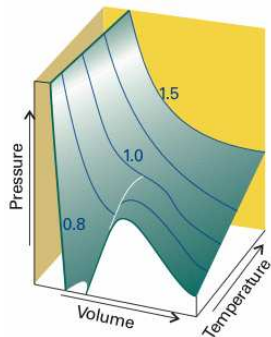
- $(dP/dV)_T > 0$ for $T < T_c$ at some volumes.
- Accessed with fixed T, V boundary conditions (“Helmholtz”).
- Mechanically unstable, : fluid breaks into two phases with different densities.
- Fixed V : Minimise the Helmholtz Free Energy.

Phase coexistence isotherm (Maxwell's Construction)

- Dotted line is unstable vdW isotherm.
- Phase coexistence is a straight line connecting the denser “liquid” less dense “vapour” phase.
- Gibbs free energy of each phase is equal.

$$\Delta g = \int vdP_T = 0$$

- Maxwell construction: Pink and purple - equal areas.

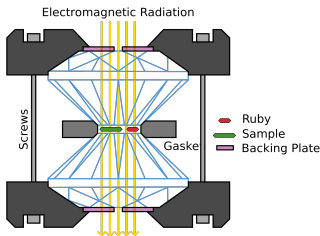


Phases and the PVT surface

Compare vdW and real phase diagram

- vdW has liquid and gas phases, critical point.
- Homogeneous: no solid phase, melt line or triple point.
- A real substance compressed slowly at constant temperature...

- a) vapour
 - b) coexistence
 - c) liquid
 - d) coexistence
 - e) solid
 - f) coexistence
 - g) high pressure solid
- goto (f)



Ross Howie, Thermodynamics 2008, cover of Nature 2015.

Projections of Equation of state

PT plane (“Gibbs”) phase boundaries.

VT plane (“Helmholtz”) shows phase coexistence.

PV plane (“indicator”) can show isotherms.

