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$U(S, V)$, $dU = TdS - pdV$ when df is an exact differential,

$$\left(\frac{\partial g}{\partial y}\right)_x = \underbrace{\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y}}_{\text{both x and y, vary}} = \left(\frac{\partial h}{\partial x}\right)_y$$

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for reversible changes in systems with no non-mechanical work

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$dG = Vdp - SdT$

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

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Thermodynamic equation of state :

$dU = TdS - pdV$

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Find for van der Waals gas., $\pi_T = a\frac{n^2}{V^2} > 0 \implies \left(\frac{\partial U}{\partial V}\right)_T > 0$
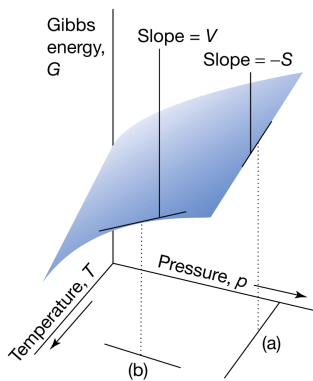
Gibbs' Free energy and entropy

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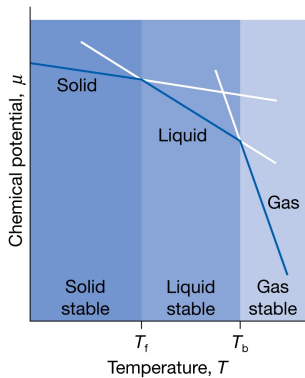
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Gibbs' Free energy and entropy

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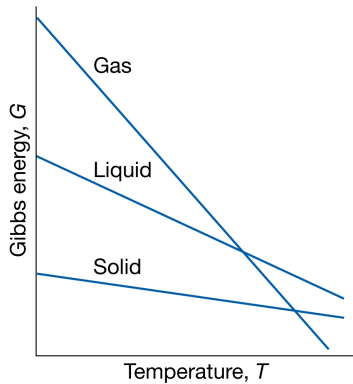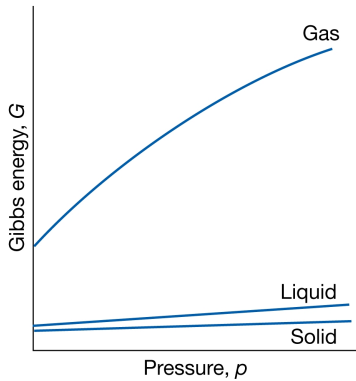
$$\left(\frac{\partial G}{\partial p}\right)_T = V > 0$$

chemical potential and phase equilibrium : $\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$

sublimation before melting

Gibbs energy, G

Gas

Liquid

Solid

Temperature, T

$$\left(\frac{\partial G}{\partial p}\right)_T = V > 0$$

Gibbs-Helmholtz equation :

$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{G - H}{T}$$

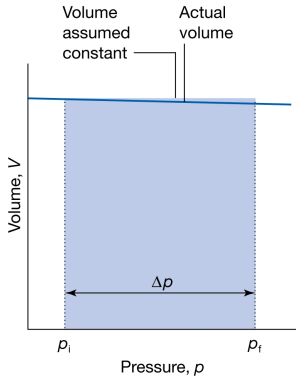Use this to show : $\left(\frac{\partial\left[\frac{G}{T}\right]}{\partial T}\right)_p = -\frac{H}{T^2}$

$$\boxed{\left(\frac{\partial\left[\frac{\Delta G}{T}\right]}{\partial T}\right)_p = -\frac{\Delta H}{T^2}}$$

Change in G with p : $G(p_f) = G(p_i) + \int\limits_{p_i}^{p_f} V dp$

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for condensed phases   gases

Volume
assumed
constant

Actual
volume

Volume, V

Δp

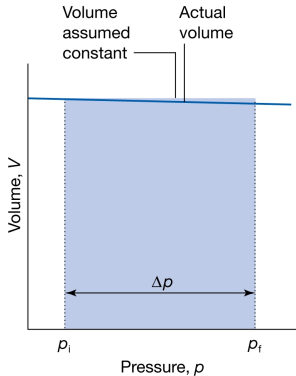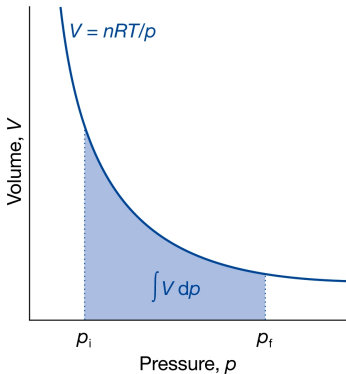p_i p_f

Pressure, p

Change in G with p : $G(p_f) = G(p_i) + \int_{p_i}^{p_f} V dp$

for condensed phases   gases

Volume assumed constant ⎯ Actual volume

Volume, V

Δp

p_i p_f

Pressure, p

$V = nRT/p$

Volume, V

$\int V\, dp$

p_i p_f

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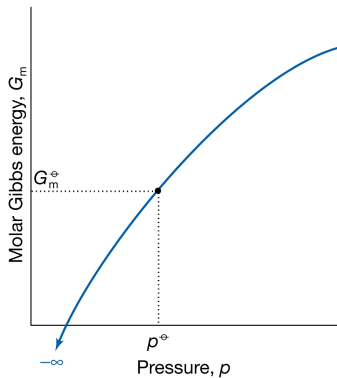p_i p_f

Pressure, p Pressure, p
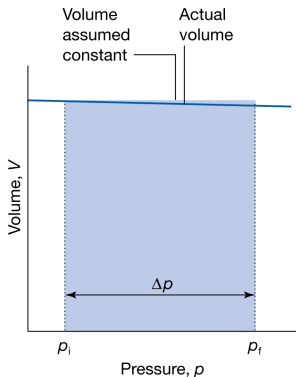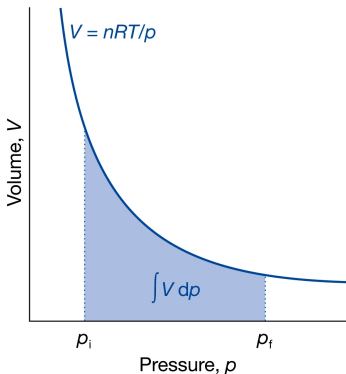
$G_m(p_f) = G_m(p_i) + V_m(p_f - p_i)$ $G_m(p_f) = G_m(p_i) + RT \int_{p_i}^{p_f} \frac{dp}{p} = G_m(p_i) + RT \ln \frac{p_f}{p_i}$

molar Gibbs energy vs p : $G_m(p) = G_m^{\ominus} + RT \ln \dfrac{p}{p^{\ominus}}$

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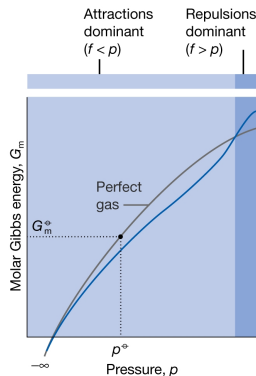
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or, $\ln \phi = \int_{0}^{p} \frac{Z-1}{p} \, dp$

Attractions dominant ($f < p$) Repulsions dominant ($f > p$)

Molar Gibbs energy, G_m

Perfect gas

G_m^*

$-\infty$

p^*

Pressure, p

phase : form of matter that is uniform throughout in chemical composition and physical state

$P = \#$ phases in a system

Phase equilibria - triple point (T_3) and critical point (T_C)
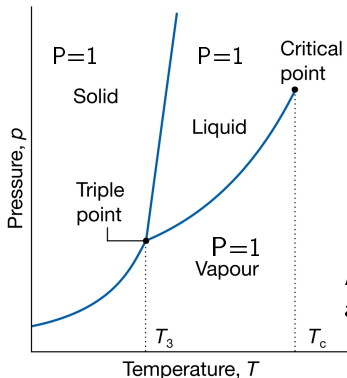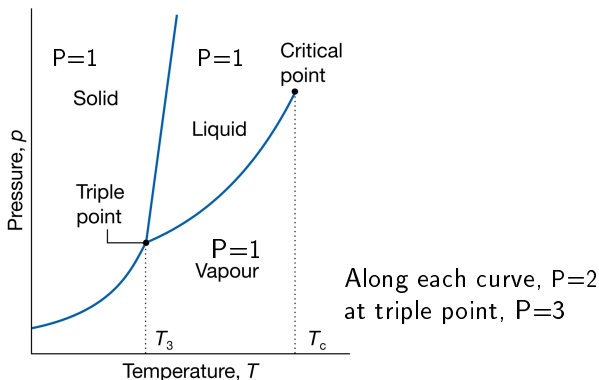

Along each curve, P=2
at triple point, P=3

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Phase equilibria - triple point (T_3) and critical point (T_C)

Along each curve, P=2
at triple point, P=3

For water : $T_3 = 273.16$ K and 611 Pa (6.11 mbar)

- ▶ Triple point marks the lowest pressure at which a liquid phase can exist
- ▶ If the slope of the solid–liquid phase boundary is positive
  - ▶ then triple point also marks the lowest temperature at which the liquid can exist
- ▶ the critical temperature is the upper limit

Phase Rule : $F = C - P + 2$

$F =$ #degrees of freedom, $C =$ #components, $P =$ #phases

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single-component, single-phase

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$F = 1 - 1 + 2 = 2$
single-component, two-phases
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single-component, two-phases
$F = 1 - 2 + 2 = 1$
phases α and β in equilibr. at given p, T
$\mu_\alpha (p, T) = \mu_\beta (p, T)$
eqn. relates p and T,
so only one variable is independent

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single-component
three-phases
$F = 1 - 3 + 2 = 0$

Phase Rule : $F = C - P + 2$

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single-component, single-phase

$F = 1 - 1 + 2 = 2$
single-component, two-phases
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single-component
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$F = 1 - 3 + 2 = 0$
phases α, β and γ in equilibr. at given p, T,
$\mu (\alpha, p, T) = \mu (\beta, p, T)$
$\quad = \mu (\gamma, p, T)$

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two eqns. for two unknowns p
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$\quad = \mu (\gamma, p, T)$
two eqns. for two unknowns p and T
fixed soln.
so no variation possible

Typical phase diagram
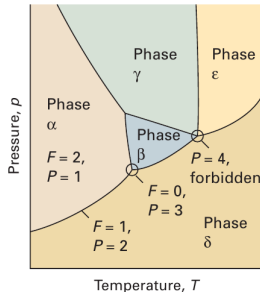
Experimental phase diagrams
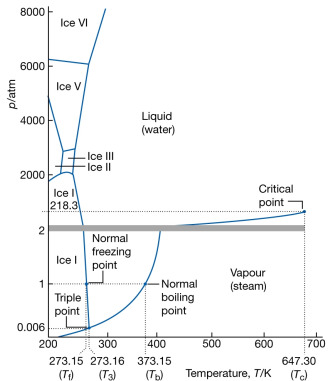
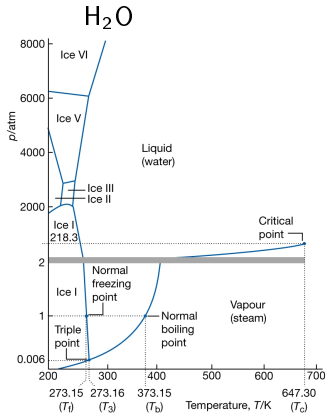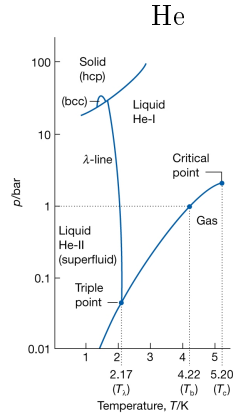## H_2O CO_2 He

Experimental phase diagrams

H_2O

CO_2

He

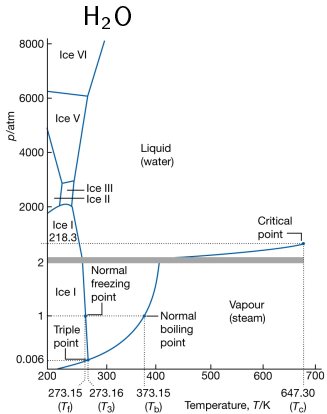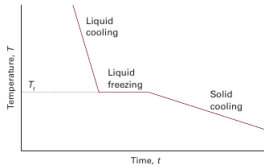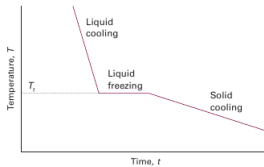# Experimental phase diagrams

H₂O

CO₂

He
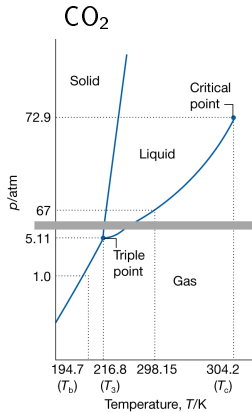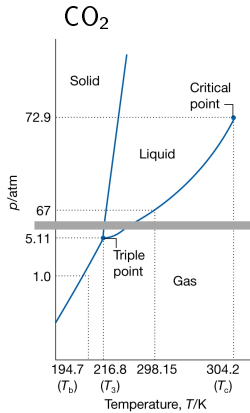
Phase transition : Thermal analysis and Cooling curve

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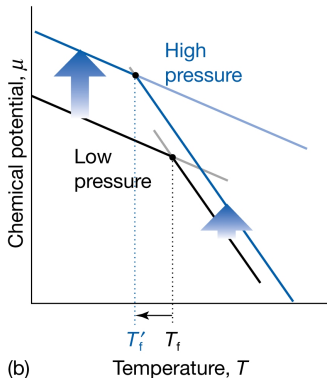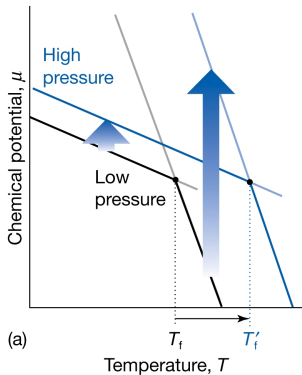metastable phases : Kinetic barriers

Response of melting to applied pressure

Response of melting to applied pressure

pressure-dependence of chemical potential : $\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$

usual liquids : $V_m(l) > V_m(s)$ water : $V_m(l) < V_m(s)$

$$G_m(p) = G_m^{\ominus} + RT \ln \frac{p}{p^{\ominus}}$$

$$\implies \mu(p) = \mu^{\ominus} + RT \ln \frac{p}{p^{\ominus}} \overset{p^{\ominus}=1}{=} \mu^{\ominus} + RT \ln p$$

location of phase boundaries : $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T = \frac{\Delta_{trs} S}{\Delta_{trs} V}$

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equilibrium is disturbed
It can be restored by changing T, moving
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It can be restored by changing T, moving
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relation between dp and dT ensures that
system remains in equilibrium as either
variable is changed

Left panel — axes: Temperature, T (x-axis); Pressure, p (y-axis). Regions labeled: Solid, Liquid.

Middle panel — axes: Temperature, T (x-axis); Pressure, p (y-axis). Regions labeled: Liquid, Gas.

Right panel — axes: Temperature, T (x-axis); Pressure, p (y-axis). Regions labeled: Solid, Liquid, Gas.