Phase equilibria of pure substances

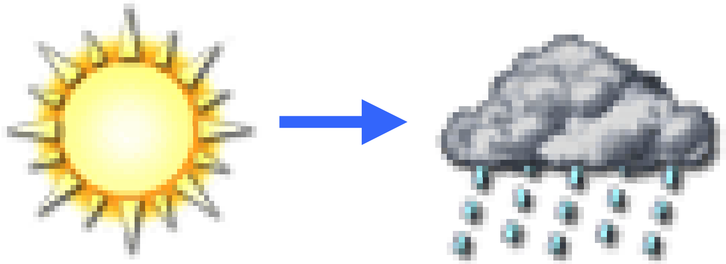
Atkins, Chapter 5

Phase transition: phase change without change in chemical composition (e.g., ice melting, evaporation + fog formation)

Molar Gibbs energy: $G_m = \frac{G}{n}$

extensive

intensive



Phase 1: water vapor

Phase 2: water liquid

A substance has a spontaneous tendency to change into the phase of lowest molar Gibbs energy

To occur spontaneously:

$$\Delta G = nG_m(2) - nG_m(1) = n\{G_m(2) - G_m(1)\} < 0$$

The Gibbs energy "under pressure"

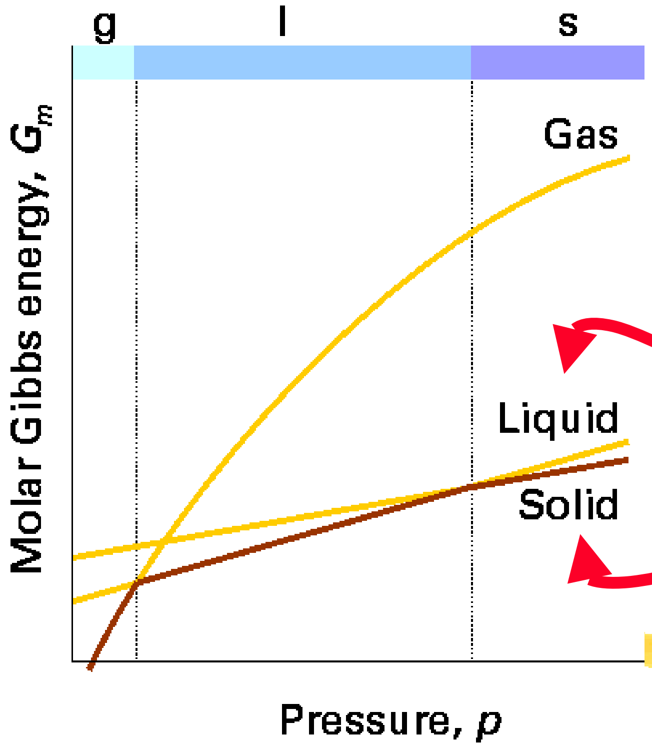
$$dG = Vdp - SdT$$

From G = H -TS ⇒ dG = dH - TdS - SdT
and dH = dU + pdV + Vdp and dU = dw + dq
and reversible change: dq = TdS and dw = -pdV

$$\Rightarrow dG_m = V_m dp - S_m dT = V_m dp$$

at constant T

With increasing pressure (dp > 0) the molar Gibbs energy increases (dG > 0)



$$\Delta G_m = \int_{p_i}^{p_f} V_m dp = V_m \int_{p_i}^{p_f} dp = V_m \Delta p$$

For liquid, solid:
V_m independent of p
⇒ linear p dependence

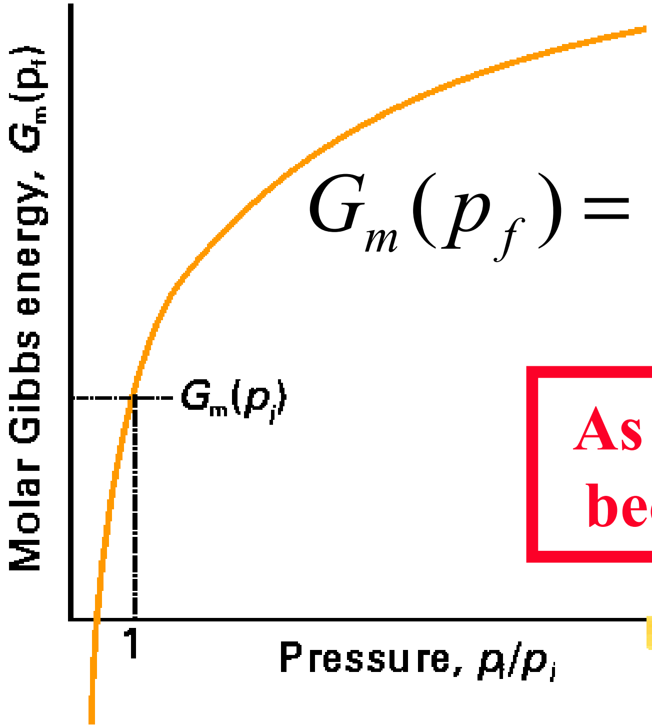
The Gibbs energy of gases under pressure

$$\Delta G_m = G_m(p_f) - G_m(p_i) = \int_{p_i}^{p_f} V_m \, dp$$

perfect gas equation

$$= \int_{p_i}^{p_f} \frac{RT}{p} dp = RT \int_{p_i}^{p_f} \frac{dp}{p} = RT \ln \frac{p_f}{p_i}$$

@ constant T



$$G_m(p_f) = G_m(p_i) + RT \ln \frac{p_f}{p_i}$$

As V_m gets smaller (@ higher p), G_m becomes less responsive to pressure

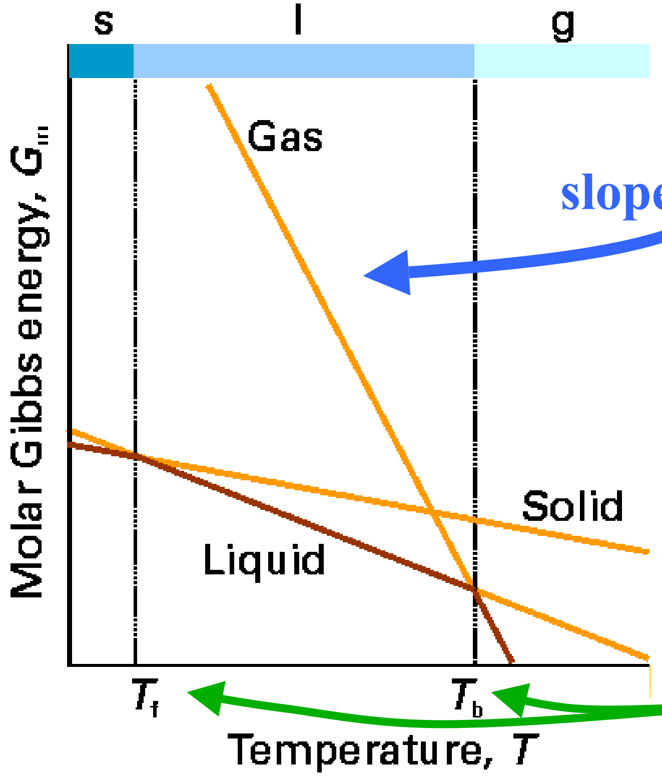
The Gibbs energy “under fire”

$$dG_m = V_m dp - S_m dT$$
$$= -S_m dT$$

@ constant p

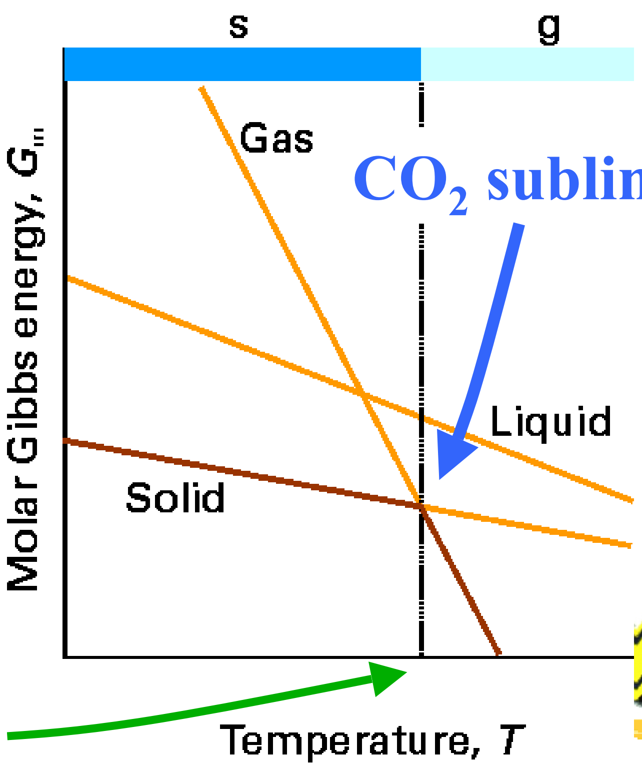
Since the molar entropy is always positive, an increase in temperature (dT > 0) always leads to a decrease in G_m ($dG_m < 0$)

S_m(gas) > S_m(liquid) > S_m(solid)



slopes

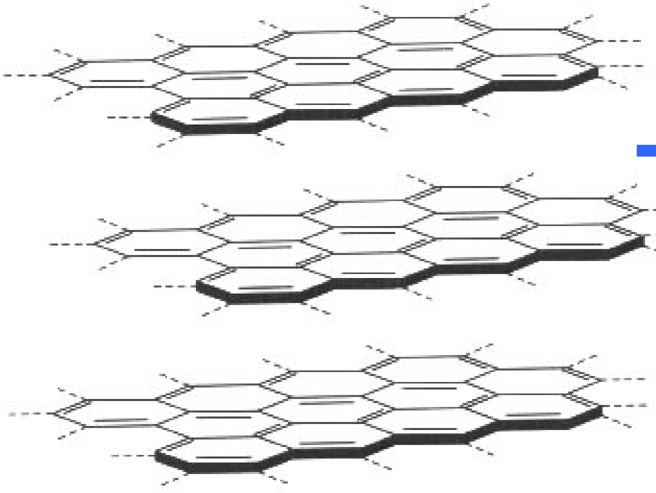
Transition temperatures



CO_2 sublimes

Luckily, there is more than thermodynamics in life

Graphite



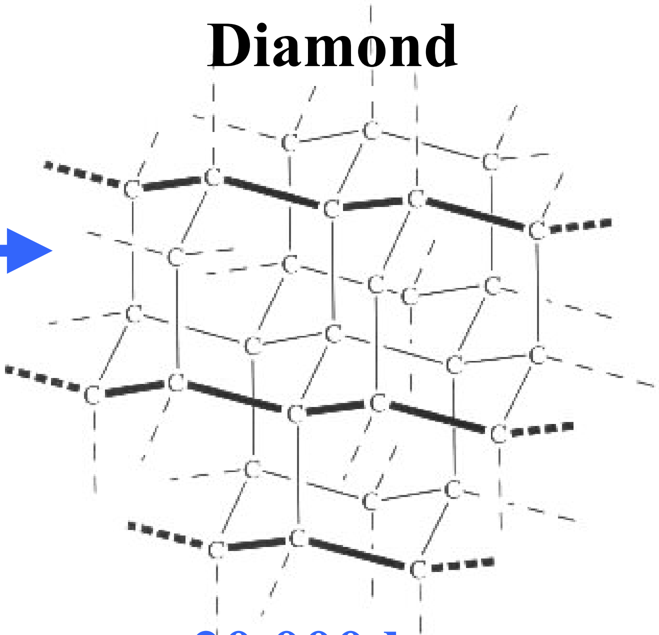
$<$20,000 bar

@ 1 bar: 3 kJ mol^{-1}

more stable

p →

Diamond



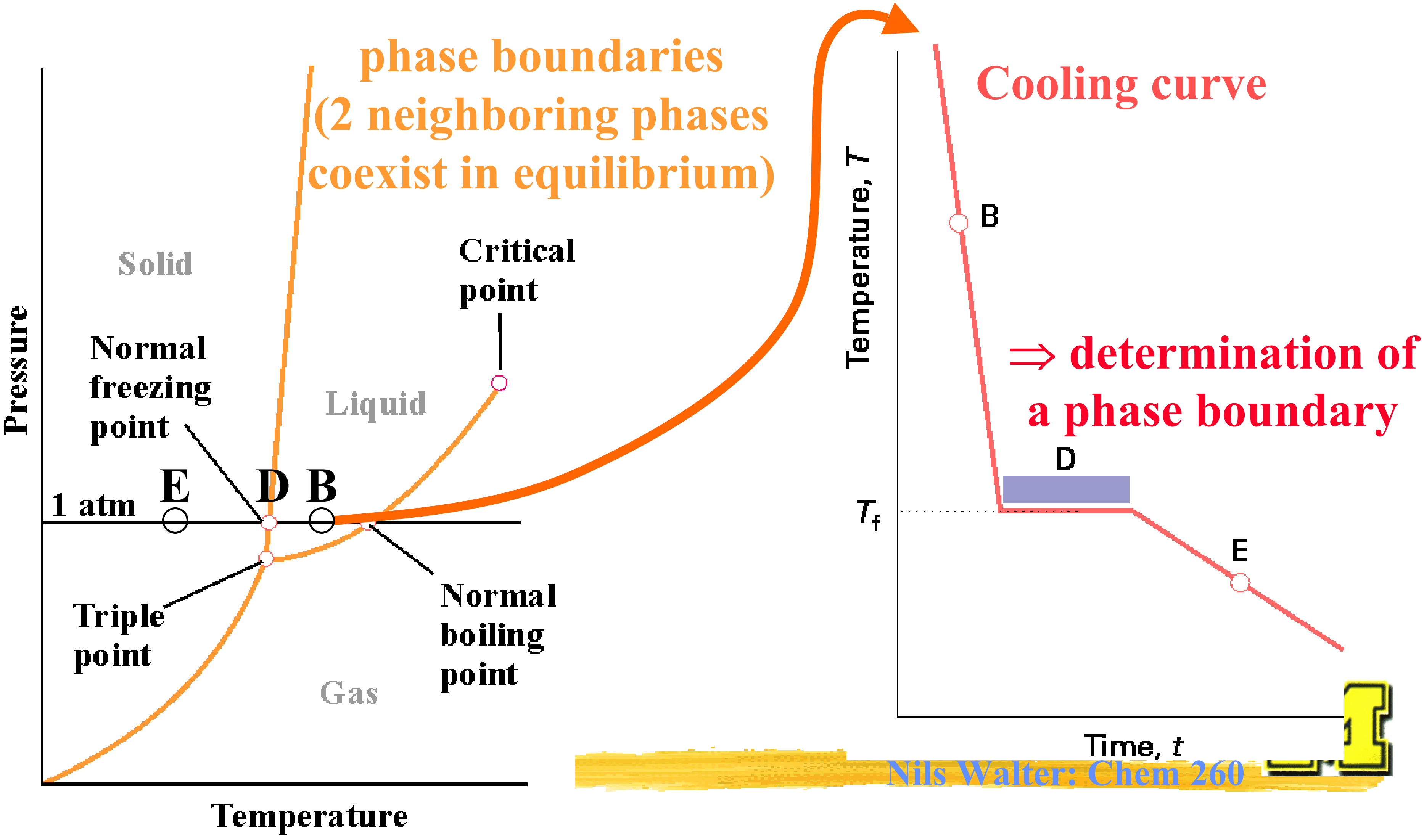
$>$20,000 bar

Slow kinetics make engagements more durable...

Spontaneity (determined by ΔG) is a tendency, not necessarily an actuality

Phase diagrams

= maps showing p, T conditions at which the various phases of a substance are stable



phase boundaries (2 neighboring phases coexist in equilibrium)

Cooling curve

⇒ determination of a phase boundary