

The third law of thermodynamics (Nernst):

The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero: $S \rightarrow 0$ as $T \rightarrow 0$ provided all the substances involved are perfectly ordered.

\Rightarrow The entropy of all perfect crystalline substances is zero at $T=0$

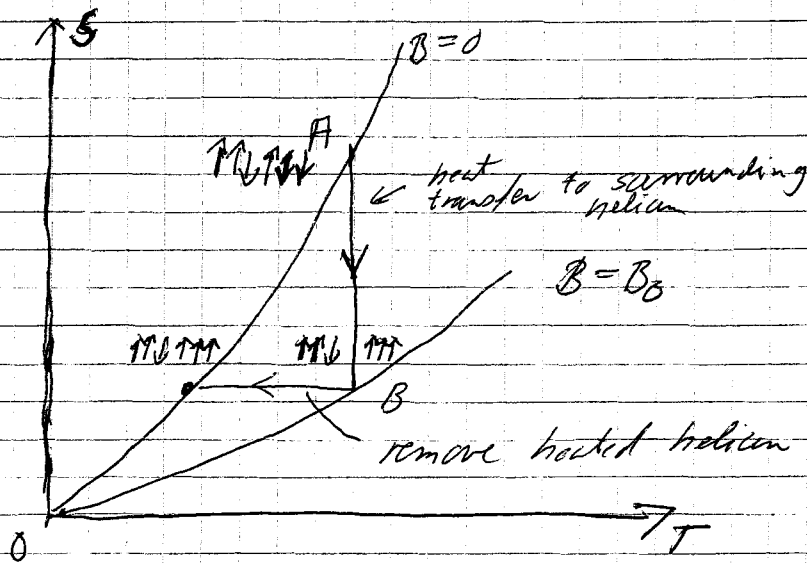
($S=0$ at $T=0$ reasonable convention)

Reaching very low temperatures

e.g. cooling of atoms, Bose-Einstein condensate

adiabatic demagnetization

paramagnetic material



Laser cooling:

in the optical trapping technique atoms in the gas phase are cooled by inelastic collisions with photons from intense laser beams, which act as walls of a very small container

The Helmholtz and Gibbs energies

equilibrium, T

$$dS - \frac{dq}{T} > 0 \begin{cases} \text{constant volume} \\ \text{constant pressure} \end{cases}$$

criteria for spontaneous change

• $V = \text{const}$ $dW_{\text{max expansion}} = 0$

$$dS - \frac{dq_v}{T} = dS - \frac{dU}{T} \geq 0$$

$dq_v = dU$

$$\Leftrightarrow T dS \geq dU$$

$$\Rightarrow dS_{\text{univ}} \geq 0 \quad dU_{S,V} \leq 0 \quad (\Leftrightarrow dS_{\text{univ}} \geq 0)$$

\Rightarrow Helmholtz energy A :

$$\boxed{A = U - TS} \Rightarrow dA = dU - T dS \quad (T = \text{const})$$

\Rightarrow spontaneous change: $dA_{T,V} \leq 0$

\Rightarrow maximum work:

the change in the Helmholtz energy is equal to the maximum work accompanying a process:

$$dW_{\text{max}} = dA$$

Proof:

Clausius $T dS \geq dq$ first law $dU = dq + dW$

$$\Rightarrow dU \leq T dS + dW$$

$$\Rightarrow dW \geq dU - T dS$$

$$\Rightarrow dW_{\text{max}} = dU - T dS = dA$$

not the total change in internal energy can be converted in work there is always a loss in form of heat

p = const.:

no work other than expansion work

$$dq_p = dH \Rightarrow T ds \geq dH$$

$$0 \geq dH - T ds$$

$$\Rightarrow dS_{H,p} \geq 0 \quad dH_{S,p} \leq 0$$

⇒ Gibbs energy G:

$$\boxed{G = H - TS} \Rightarrow dG = dH - T ds \quad (T = \text{const})$$

$$\Rightarrow \text{spontaneous change: } dG_{T,p} \leq 0$$

more interesting in demostory since in a laboratory there is usually p = const V = const

At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy

Maximum non-expansion work: $\boxed{dW_{add,max} = dG}$

Proof: $dH = dq + dw + d(pV)$

$$dG = dH - T ds - SdT = dq + dw + d(pV) + T ds - SdT$$

= 0 isothermal

reversible $dw = dw_{rev} \quad dq = dq_{rev} = T ds$

$$dG = T ds - dw_{rev} + d(pV) - T ds = dw_{rev} + d(pV)$$

≡ p dV + V dp

$$dG = (-p dV + dW_{add,rev}) + p dV + V dp = dW_{add,rev} + V dp$$

p = const T = const

$$\Rightarrow dG = dW_{add,rev} !$$

Potential exercises

4.24, 4.25, 4.23, 4.16,

Potential problems:

4.21, 4.23, 4.25, 4.10, 4.4

$dU = dq + dw$

$dW_{\text{non-exp}} = -p dV$
no non-expansion work

$dq_{\text{rev}} = T dS$

$\Rightarrow \boxed{dU = T dS - p dV}$

applies to any change - reversible or irreversible -
of a closed system that does no additional
non-expansion work

$dU = T dS - p dV = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV$
 $\qquad \qquad \qquad = T \qquad \qquad \qquad = -p$

T = const, G(p) ?

$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V dp$

• liquids and solids:

$dV \approx 0$

$\boxed{G(p_f) = G(p_i) + V \Delta p}$

normal laboratory conditions $V \Delta p \approx 0$

$\boxed{G(p_f) \approx G(p_i)}$

gases:

$$G(p_+) = G(p_i) + nRT \int_{p_i}^{p_+} \frac{dp}{p} = G(p_i) + nRT \ln \frac{p_+}{p_i}$$

\downarrow
 $V = \frac{nRT}{p}$ perfect gas

non-ideal gas:

$$G(p_+) = G(p_i) + nRT \ln \frac{f_+}{f_i}$$

fugacity: $f = \phi p$ with fugacity coefficient ϕ

$$\ln \phi = \int_0^p \frac{z-1}{p} dp$$

potential exercises:

- 5.4, 5.10, 5.14, 5.15

potential problems:

- 5.10, 5.17, 5.18, 5.20, 5.26

5. Phase Diagrams

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A phase of a substance is a form of matter that is uniform throughout in chemical composition and physical state. (various solid phases, liquid, gas)

~~Order~~

Landau: Phases can be distinguished by their degree of order
⇒ ~~order~~ introduces concept of order parameter

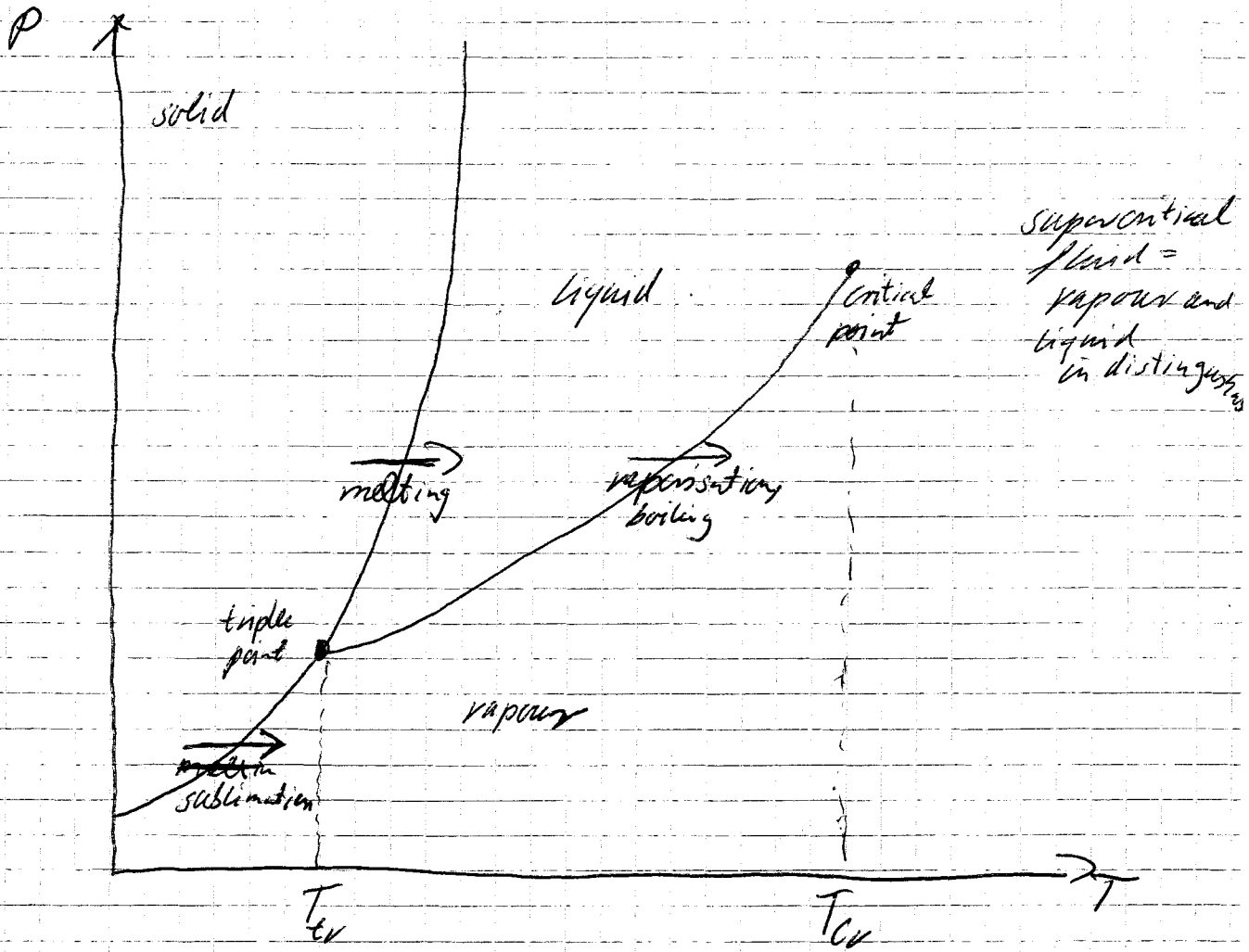
A phase transition is the spontaneous conversion of one phase into another phase.

Note: transition can be infinitely slow
⇒ metastable states

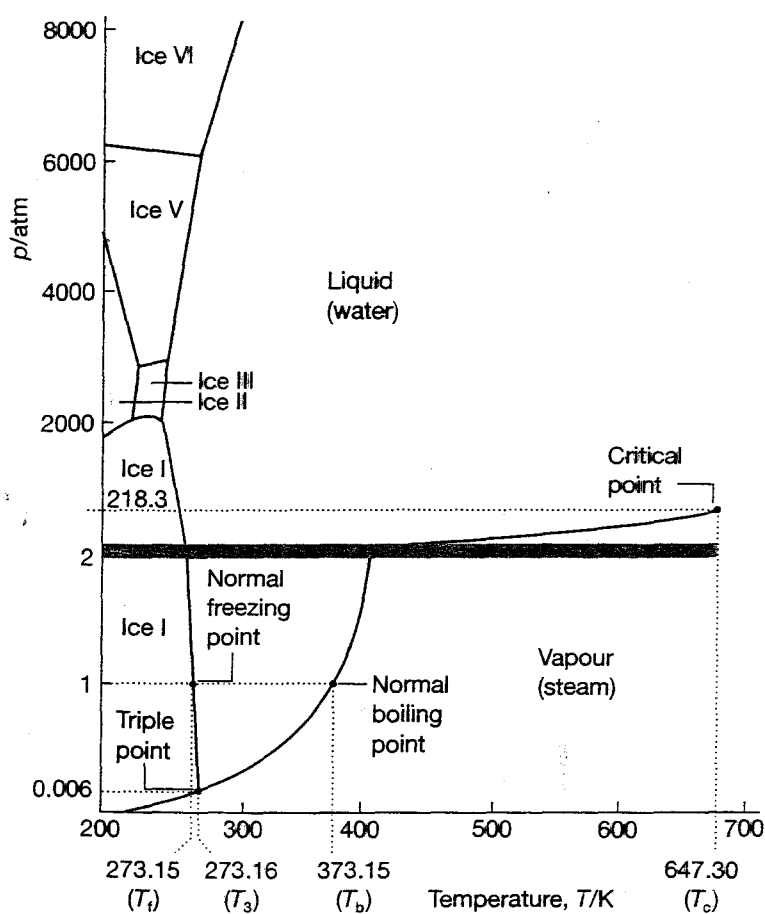
e.g. diamonds are not forever!

diamond → graphite
↑ metastable

typical phase diagrams (e.g. CO₂)



different phase diagram of water
due to H-bonds!



6.4 The experimental phase diagram for water showing the different solid phases. Note the change of vertical scale at 2 atm.

varies with the pressure. Its very steep slope indicates that enormous pressures are needed to bring about significant changes. Notice that the line has a negative slope up to 2 kbar, which means that the melting temperature falls as the pressure is raised. The reason for this almost unique behaviour can be traced to the decrease in volume that occurs on melting, and hence it being more favourable for the solid to transform into the liquid as the pressure is raised. The decrease in volume is a result of the very open molecular structure of ice: the H_2O molecules are held apart as well as together by the hydrogen bonds between them, but the structure partially collapses on melting, and the liquid is denser than the solid.

At high pressures, different structural forms of ice come into stability as the hydrogen bonds between molecules are modified by the stress. Some of these phases (which are called ice II, III, V, VI, and VII) melt at high temperatures.² Ice VII, for instance, melts at 100°C but exists only above 25 kbar. Note that five more triple points occur on the diagram other than the one where vapour, liquid, and ice I coexist. Each one occurs at a definite pressure and temperature that cannot be changed.