4. Phase Changes

19th March

Last lecture

- For gas $dW = -PdV$ - path dependent
  e.g isothermal $dW = (Nk_BT) \ln(V_0/V_1)$,
  isobaric (followed by isochoric) $dW = (Nk_BT) (1 - V_1/V_0)$

- Heat capacity (HC) define $dQ = C\,dT$
  (also path dependent)
  (molar HC, $dQ = N_m\,C_m\,dT$, specific HC, $dQ = m\,c\,dT$)

- For ideal gas, $\quad C_v = (n_d/2)\,Nk_B$ $(C_{vm} = n_d/2\,R)$
  $\qquad\qquad\qquad C_p = C_v + Nk_B$ $(C_{pm} = C_{vm} + R)$

- Adiabatic equation of state $PV^\gamma = $ constant,
  where $\gamma = C_p / C_v$
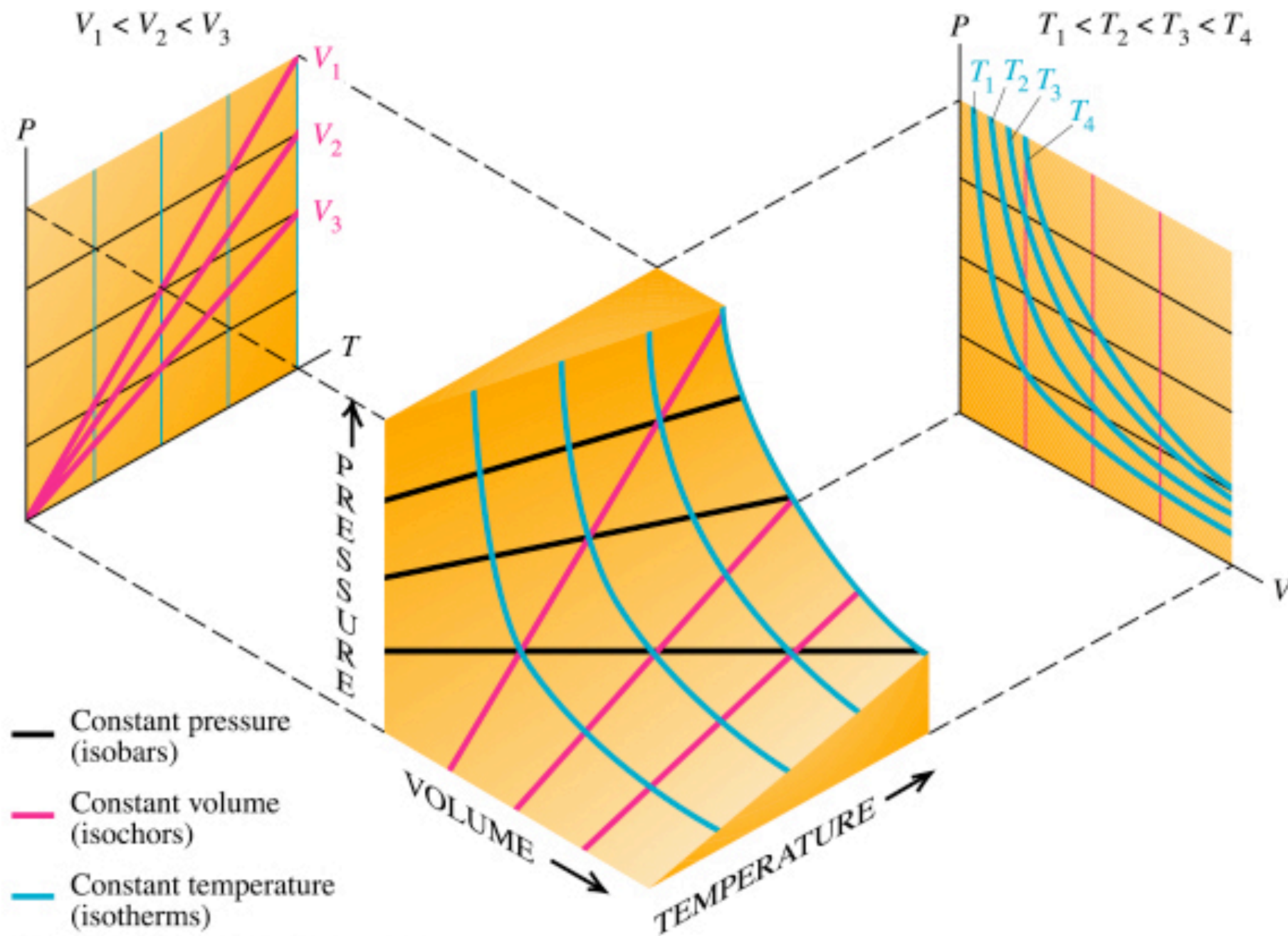
Phase Change: Definition

Phase Change = A large change in one state variable (e.g. n) for a small corresponding change in another (e.g. T).

Phase Changes usually indicate a change in internal order, and not restricted to changes of state.

(other examples, superconductivity, magnetism, crystal structure)
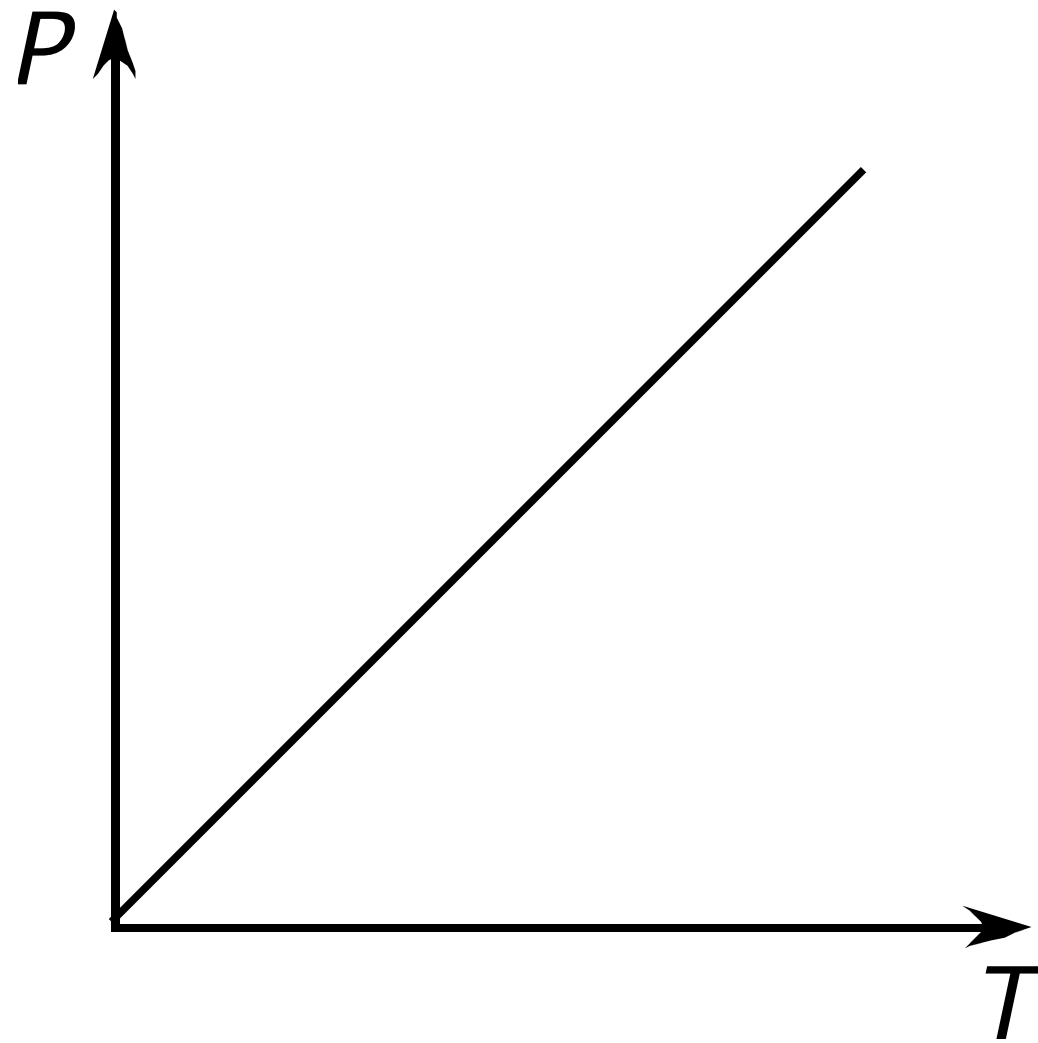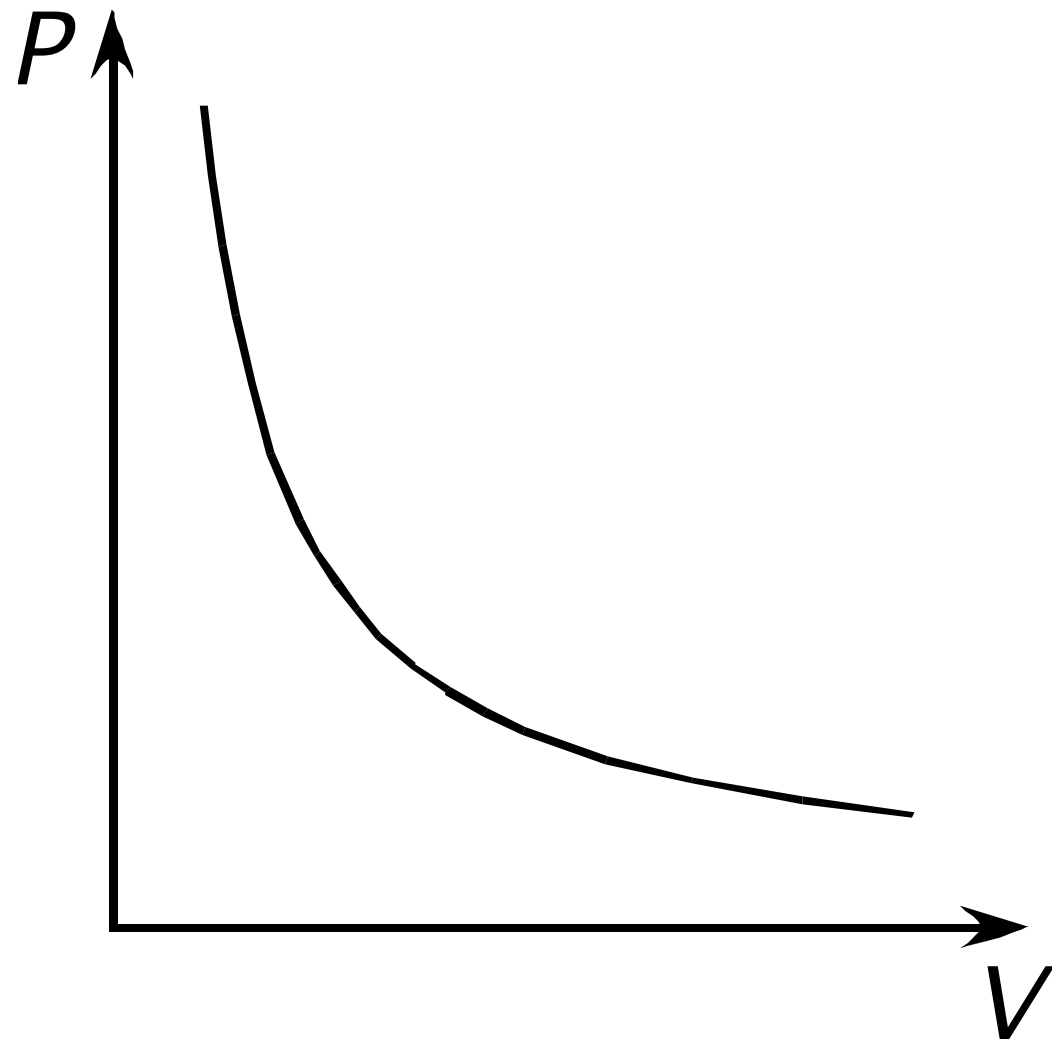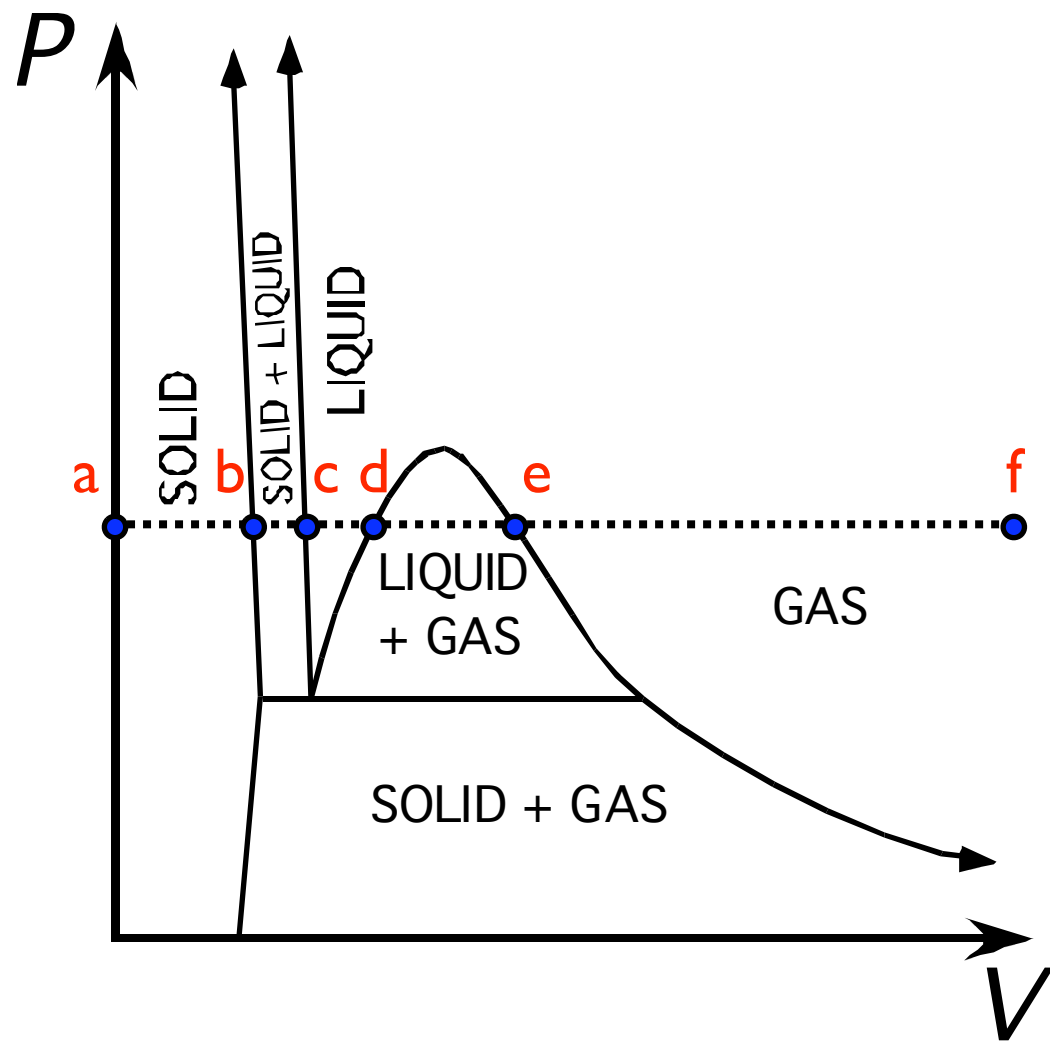
4.1 PVT surface for ideal gas

PVT ideal gas

$V_1 < V_2 < V_3$

V_1
V_2
V_3

P

T

$T_1 < T_2 < T_3 < T_4$

P

T_1 T_2 T_3
T_4

V

PRESSURE

VOLUME

TEMPERATURE

—— Constant pressure
(isobars)

—— Constant volume
(isochors)

—— Constant temperature
(isotherms)

PT projection

Figure 2

PV projection
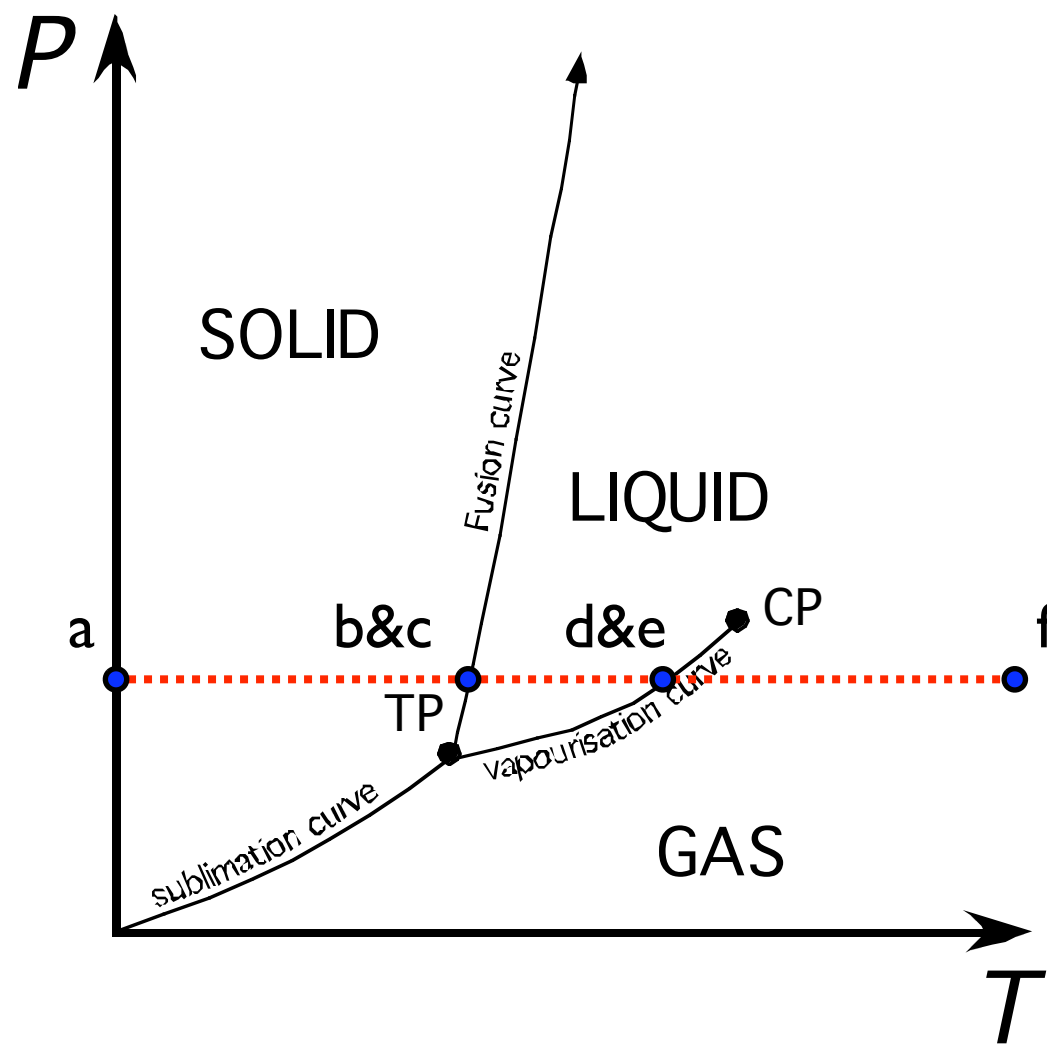

Figure 3

4.2 PVT surface for real substance

Figure 4

PT projection

a→b: solid T rises
b: starts to melt
b→c: solid / liquid co-exist, T const.
c→d: liquid, T rises
d: starts to vapourise
d→e: liquid / gas coexist, T const.
e→f: gas, T rises

Figure 5

4.3 isotherms for real substance

Isotherms on PT projection
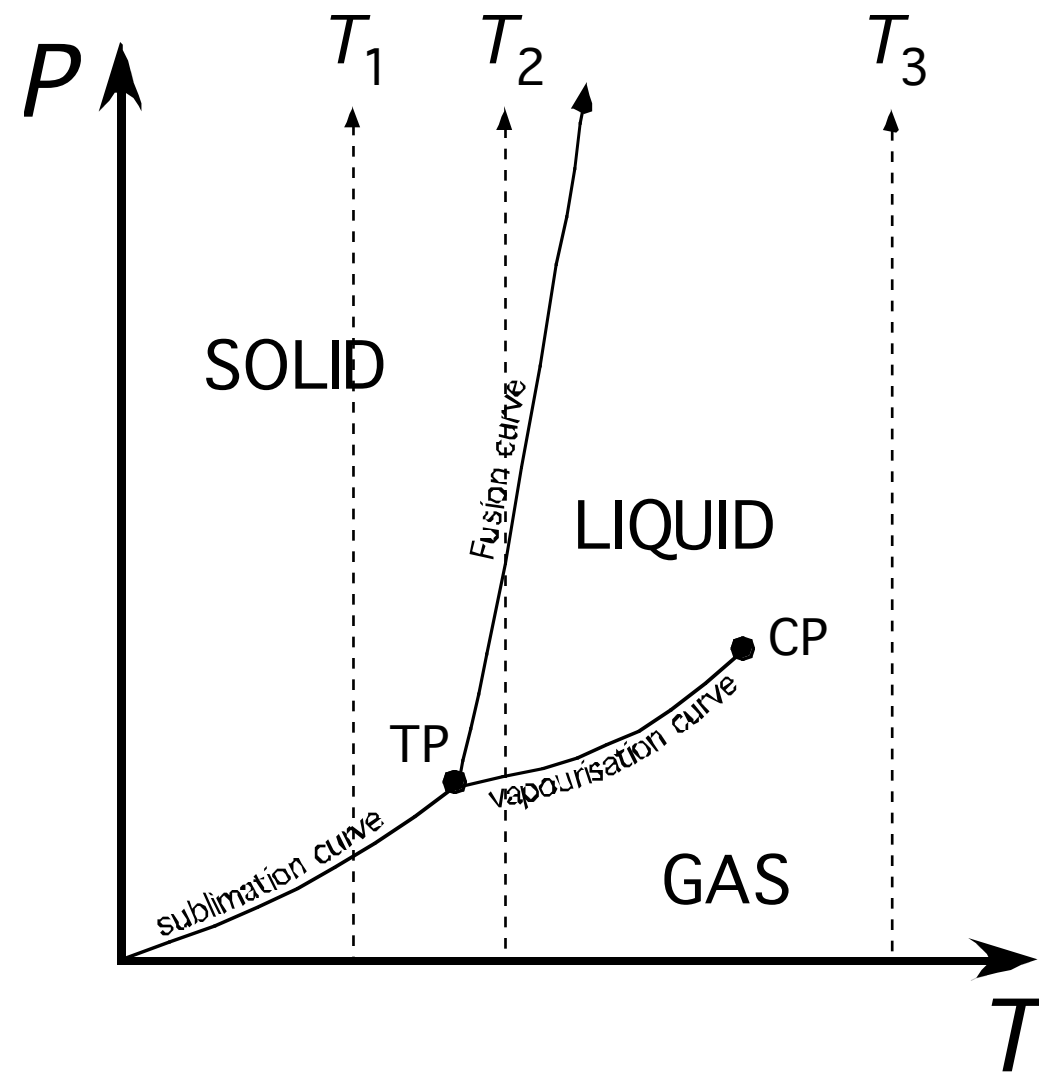
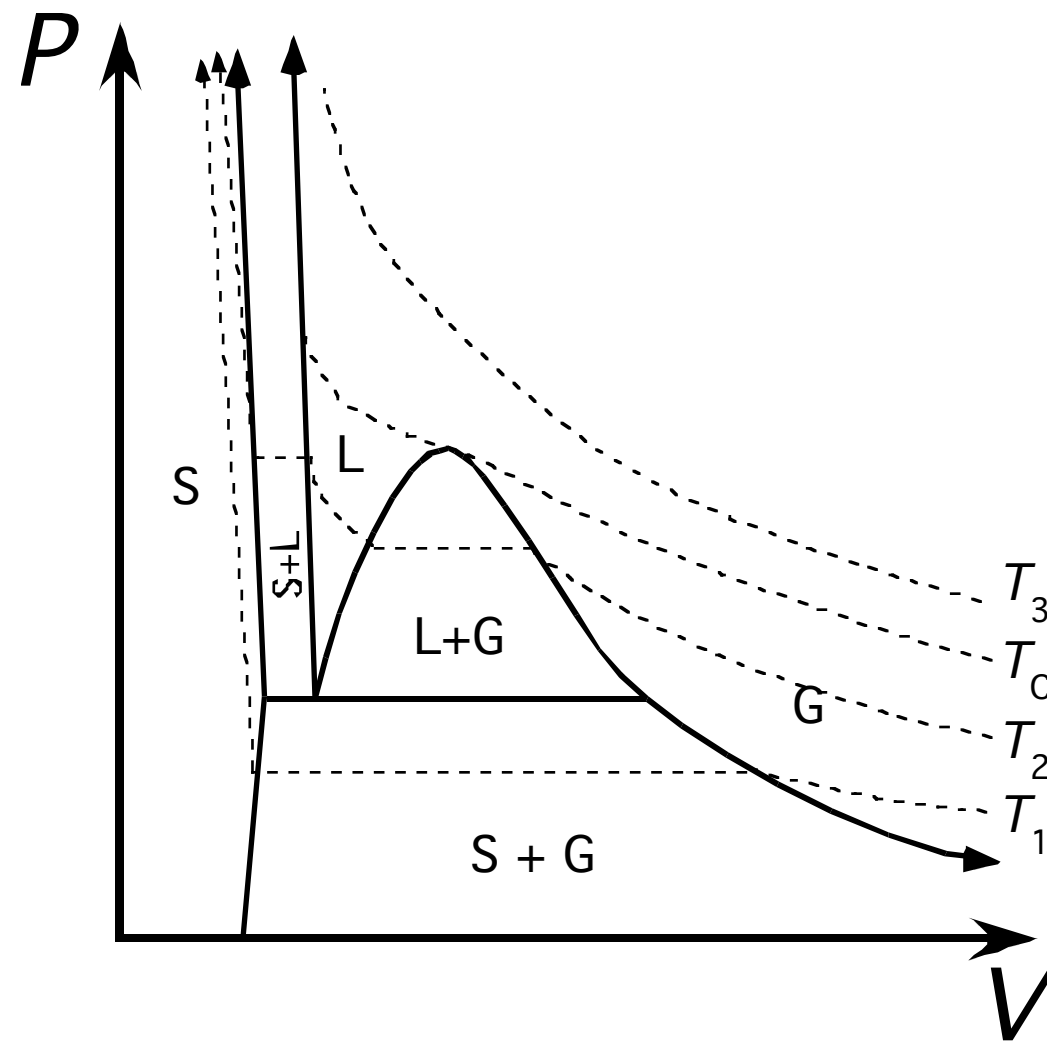Figure 6

Isotherms on PV projection
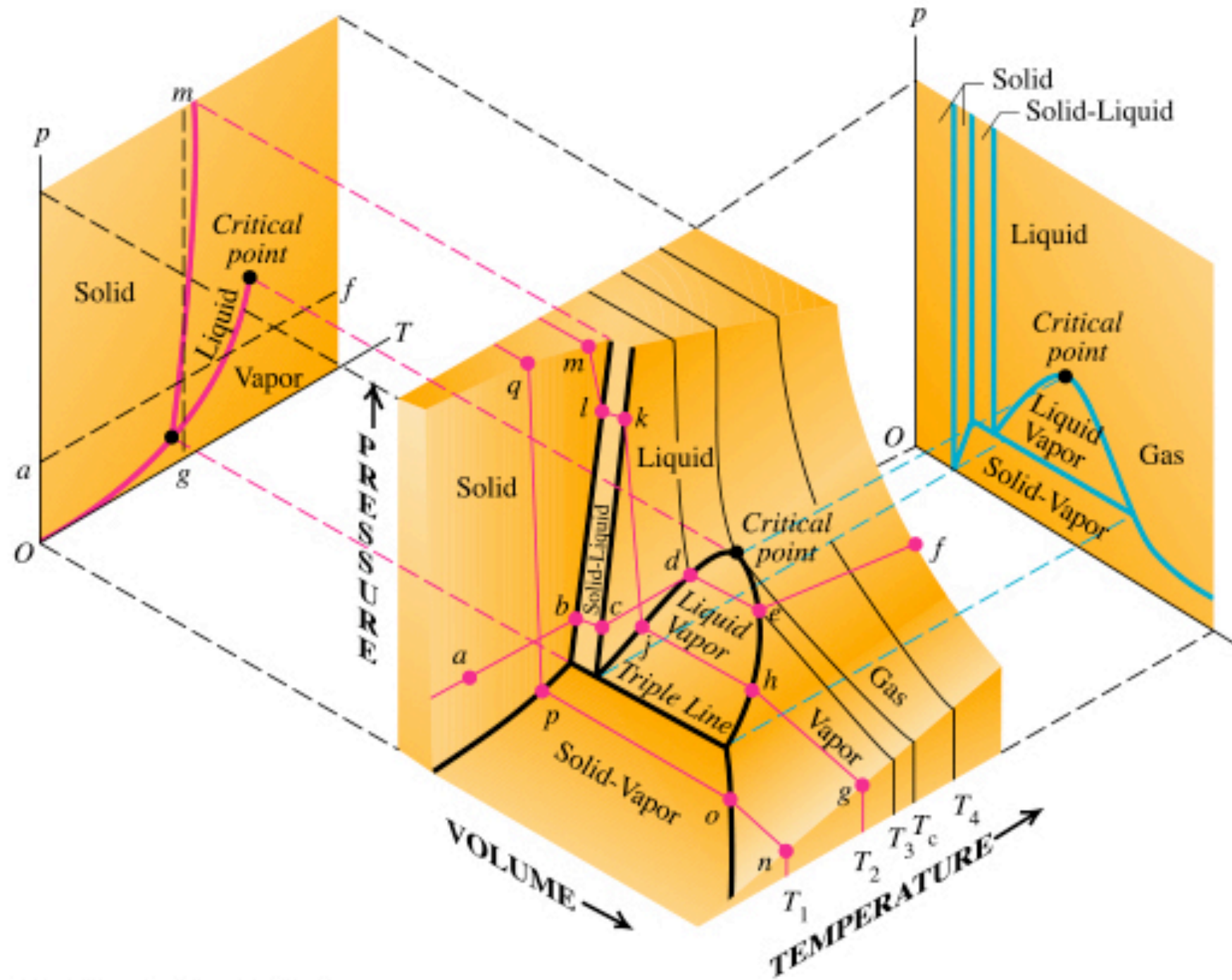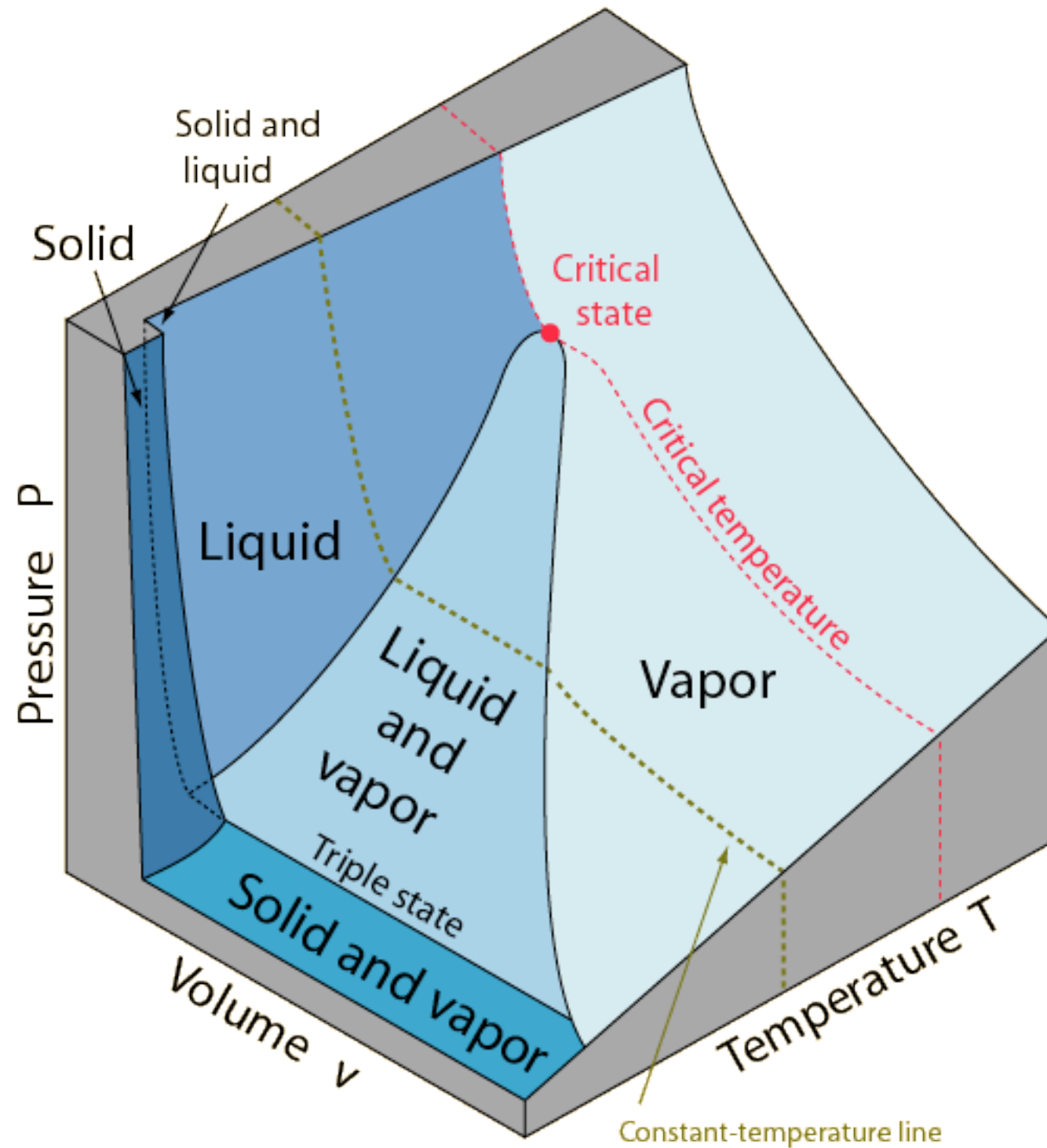

Figure 7

PVT real gas

Figure 8

4.4 Phase Changes for H$_2$0

PVT diagram for ice

PT projection H₂0
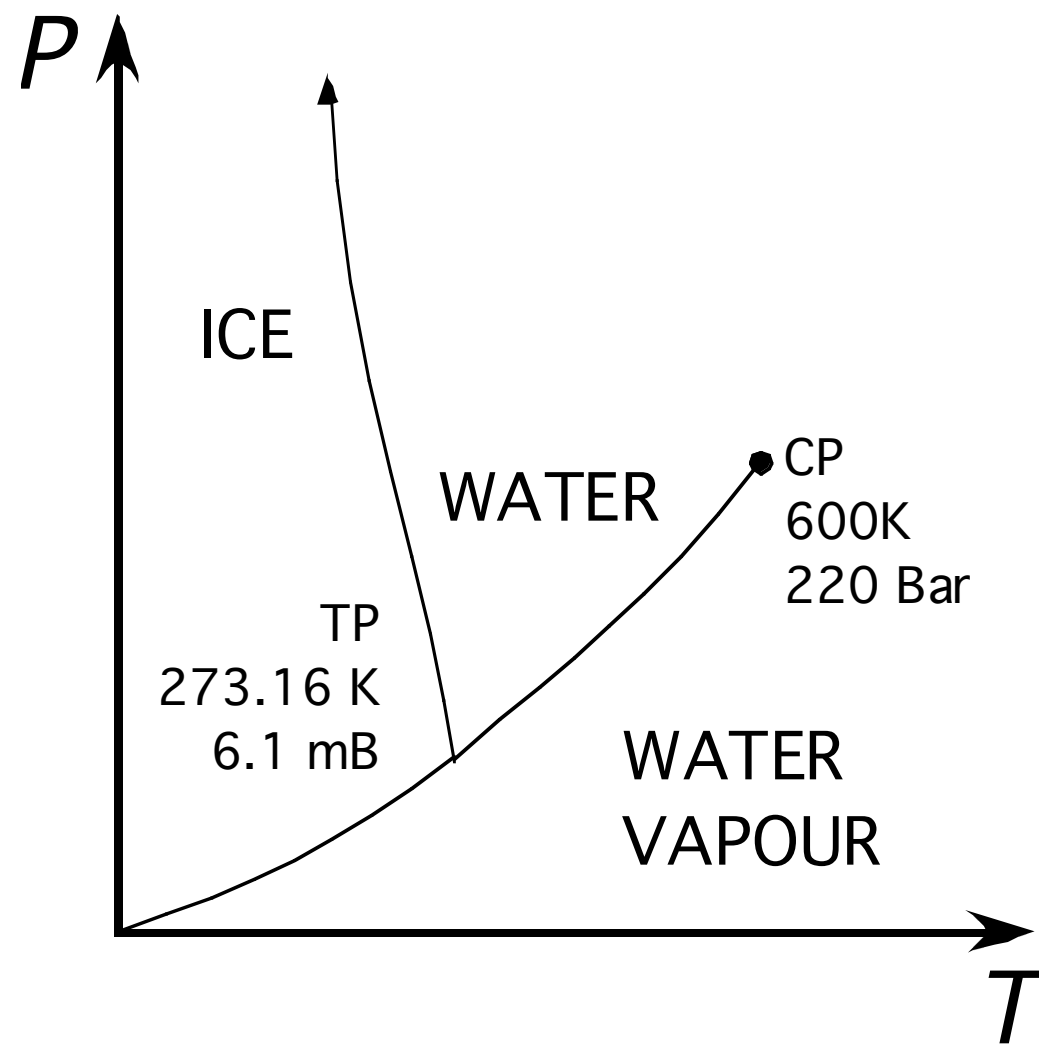
Figure 9

PVT diagram for ice
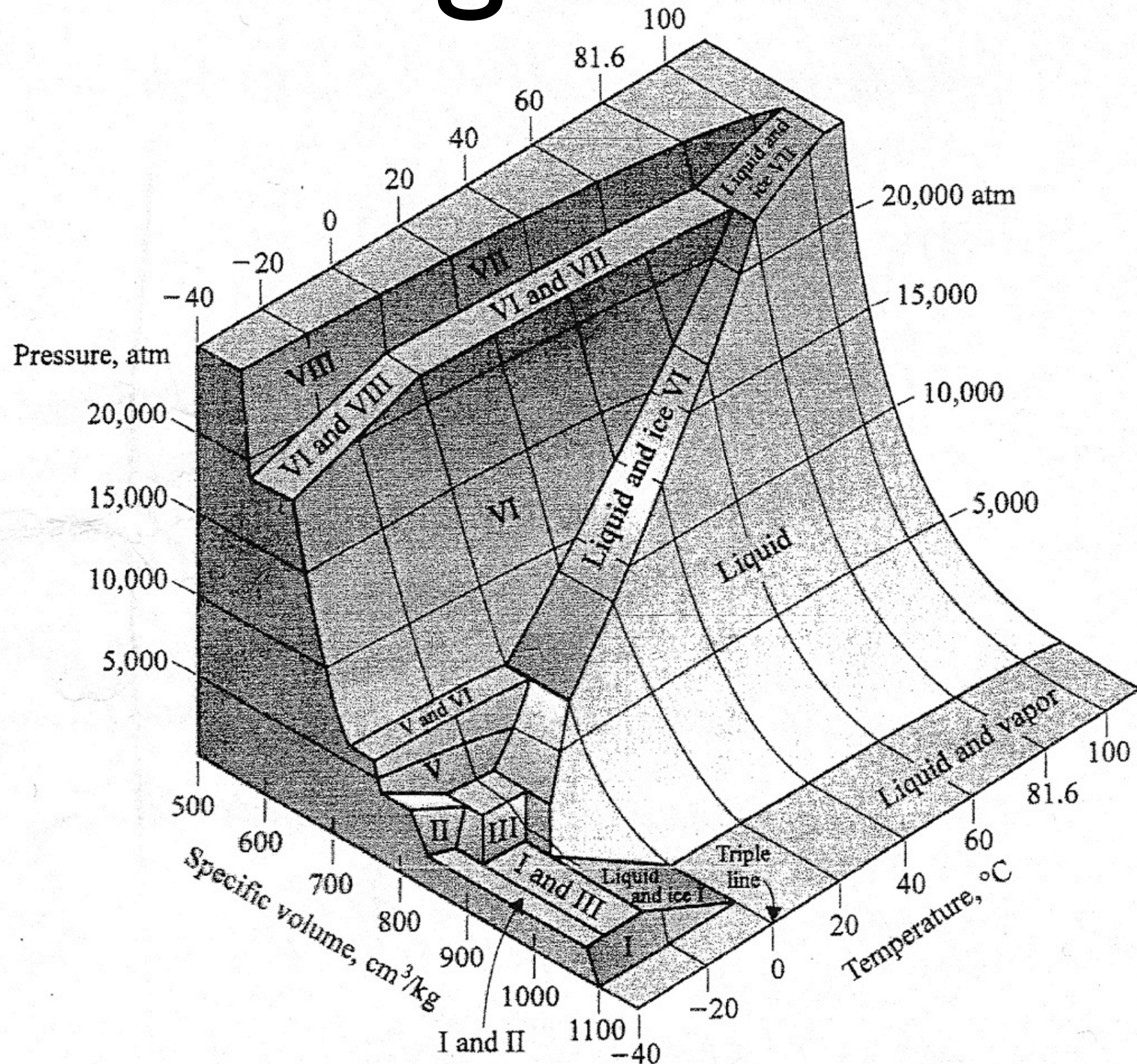
4.5 Latent heats

Change between phases is not instantaneous. Region exists in PT diagram where phases can coexist, whilst heat is entering or leaving the system at the same temperature. Heat required to cause complete change between phases = latent heat.

Latent heat of vaporisation L_v = heat required to change a liquid to a gas

Latent heat of fusion L_f = heat required to change solid to liquid

Latent heat of sublimation L_s = heat required from solid to gas for $T < T_p$ or $T > T_c$

Bond strengths & latent heat

Bond strength ϵ related to L_s ($\approx L_f + L_v$ if melting and boiling points are close.)

$$L_s = \tfrac{1}{2} N_0 n \epsilon$$

where $N_0 =$ number of molecules, $n =$ number of nearest neighbours and the $\tfrac{1}{2}$ is because each bond is shared.

Also $L_v/10 \gtrsim L_f \gtrsim L_v/30$
because melting corresponds to breaking of $\sim 0.5 - 1$ bond, as opposed to $n \gtrsim 11$ for evapouration.

Substance	ε (J)	L_{sm} (J mol^{-1})	
		Calculated	Observed
He	0.9×10^{-22}	320	90
Ne	4.8×10^{-22}	1700	1300
Ar	16.5×10^{-22}	5900	7600
Kr	25×10^{-22}	9000	10500
H$_2$	4×10^{-22}	1400	1050
N$_2$	13×10^{-22}	4700	5460

Substance	ε (J)	Temperature		
		$T = \frac{2}{3}\varepsilon/k_B$	Melting	Boiling
He	0.9×10^{-22}	4.35		4.32
Ne	4.8×10^{-22}	23.19	24.63	27.23
Ar	16.5×10^{-22}	79.71	83.55	87.34
Kr	25×10^{-22}	120.77	116.15	121.45
H_2	4×10^{-22}	57.97 *	13.84	20.26
N_2	13×10^{-22}	188.41*	63.18	77.34

* Using n_d = 7, then T_H = 24.8, T_N = 80.7

Happy Easter!