Clausius-Clapeyron equation

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The Clausius–Clapeyron relation, named after Rudolf Clausius and Benoît Paul Émile Clapeyron, is a way of characterizing a discontinuous phase transition between two phases of matter of a single constituent. On a pressure–temperature (*P*–*T*) diagram, the line separating the two phases is known as the coexistence curve. The Clausius–Clapeyron relation gives the slope of the tangents to this curve. Mathematically,

$$\frac{dP}{dT}=\frac{\Delta S}{\Delta V}=\frac{L}{T\Delta V}$$

The derivation of this equation was a remarkable early accomplishment of thermodynamics. Both sides of this equation are easily determined experimentally. The equation has been verified to high precision.

1. Phase diagram of water

The P-V phase diagram of the water is shown below.

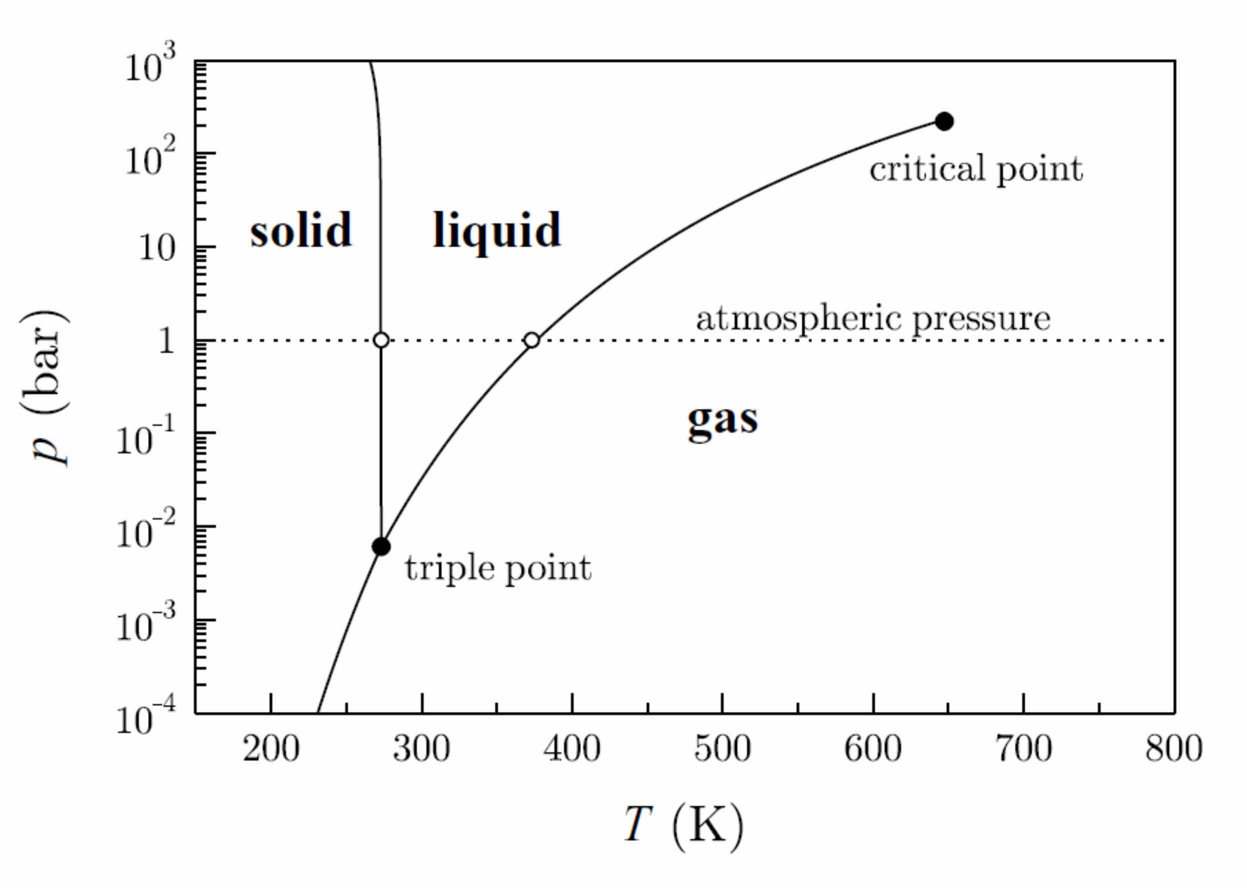


Fig. The phase diagram of H_2O showing the solid (ice), liquid (water) and gaseous (vapor) phases. The horizontal dashed line corresponds to atmospheric pressure, and the normally experienced freezing and boiling points of water are indicated by the open circles.

Critical point:

$T_c = 647.1$ K, $P_c = 218$ atm $= 22.08$ MPa

Triple point:

$T_{tr} = 273.16$ K $P_{tr} = 4.58$ Torr$= 0.00602632$ atm

The phase diagram of H_2O is divided into three regions, indicating the conditions under which ice, water, or stream, is the most stable phase. A phase diagram of water shows the solid, liquid and gaseous phases. The three phases coexist at the **triple point**. The solid-liquid phase boundary is very steep, reflecting the large change in entropy in going from liquid to solid and the very small change in volume. This phase boundary does not terminate, but continues indefinitely. By way of contrast, the phase boundary between liquid and gas terminates at the **critical point**.

((H_2O**))**
Latent heat at gas-liquid transition

$$L_0 = \begin{cases} 2485\ \text{J/g} = 44.73\ \text{kJ/mol} & \text{at}\ 0\ \text{C} \\ 2264.76\ \text{J/g} = 40.77\ \text{kJ/mol} & \text{at}\ 100\ \text{C} \end{cases}$$

1 cal = 4.184 J, H_2O = 18 g/mol

$L_0 = 2264.76$ J/g $= 9.7228$ kcal/mol $= 540$ cal/g

Phase diagram of H_2O

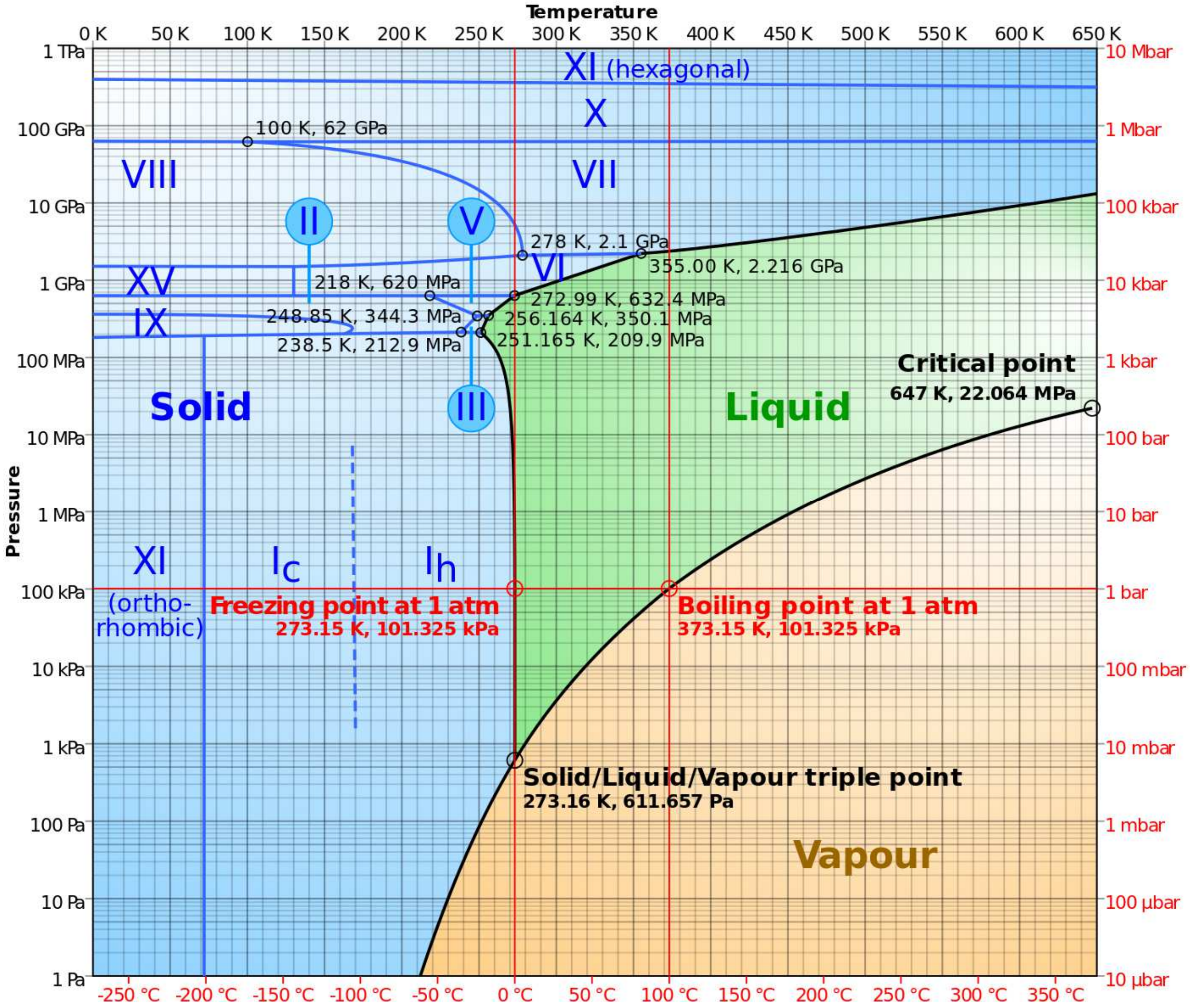
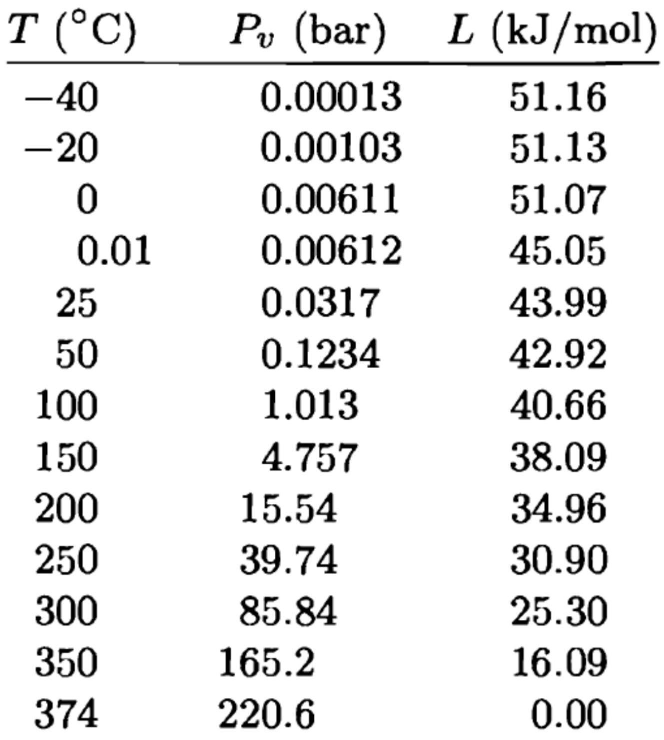


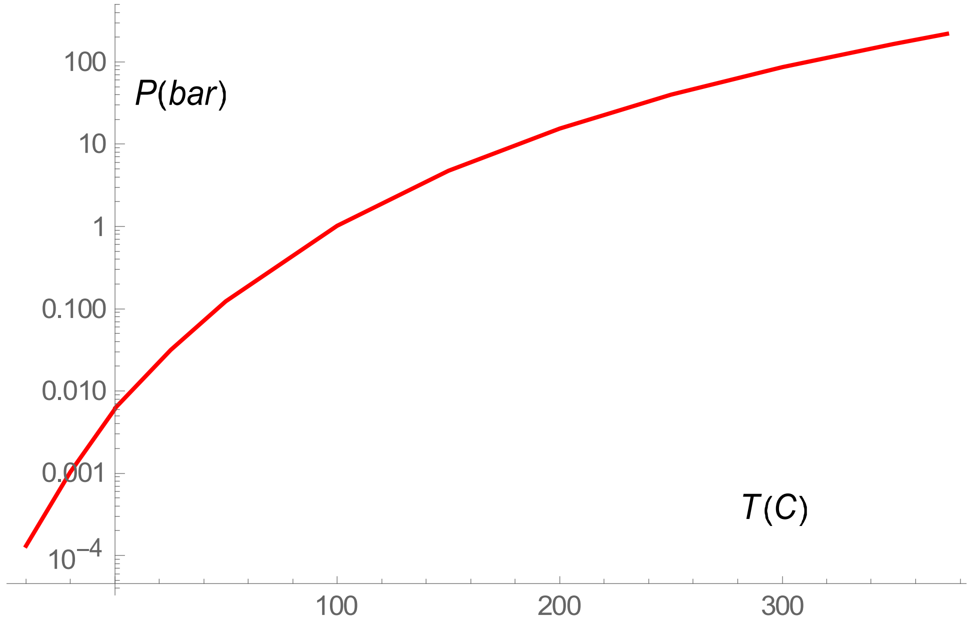
Fig. Phase diagram of water. 1 atm = 1.01325 x 10^5 Pa = 1.01325 bar. Critical point (647.1 K, 218 atm). Triple point (273.16 K, 4.58 Torr).

https://en.wikipedia.org/wiki/Phase_diagram



T (°C)	P_v (bar)	L (kJ/mol)
−40	0.00013	51.16
−20	0.00103	51.13
0	0.00611	51.07
0.01	0.00612	45.05
25	0.0317	43.99
50	0.1234	42.92
100	1.013	40.66
150	4.757	38.09
200	15.54	34.96
250	39.74	30.90
300	85.84	25.30
350	165.2	16.09
374	220.6	0.00

Table: The vapor pressure and molar latent heat for the solid-gas transformation (first three entries) and the liquid-gas transformation (remaining entries). Data from Keenan et al. (1978) and Lide (1994).



2. Derivation of Clausius-Clapeyron equation from the Carnot cycle (Adkins)

Typical curves for the *P*-*T* phase diagram in the van der Waaks gas are sketched below. Two temperatures are taken to be close together, $T_1 = T + \Delta T$ and $T_2 = T$. Now we can carry out a Carnot cycle using these two neighboring isotherms. Starting at 1, where the system is just all liquid and the temperature is $T_1 = T + \Delta T$, the cycle is as follows.

1→2: isothermal expansion during which the liquid evaporates. The evaporation requires latent heat, so that the heat Q_1 is absorbed in the system.

2→3: A small adiabatic expansion during which the temperature falls by the small amount dT; $T_2 = T$

3→4: An isothermal compression to the point where all the vapor is condensed. Latent heat Q_2 is rejected.

4→1: A small adiabatic compression during which the temperature rises by ΔT back to $T_1 = T + \Delta T$

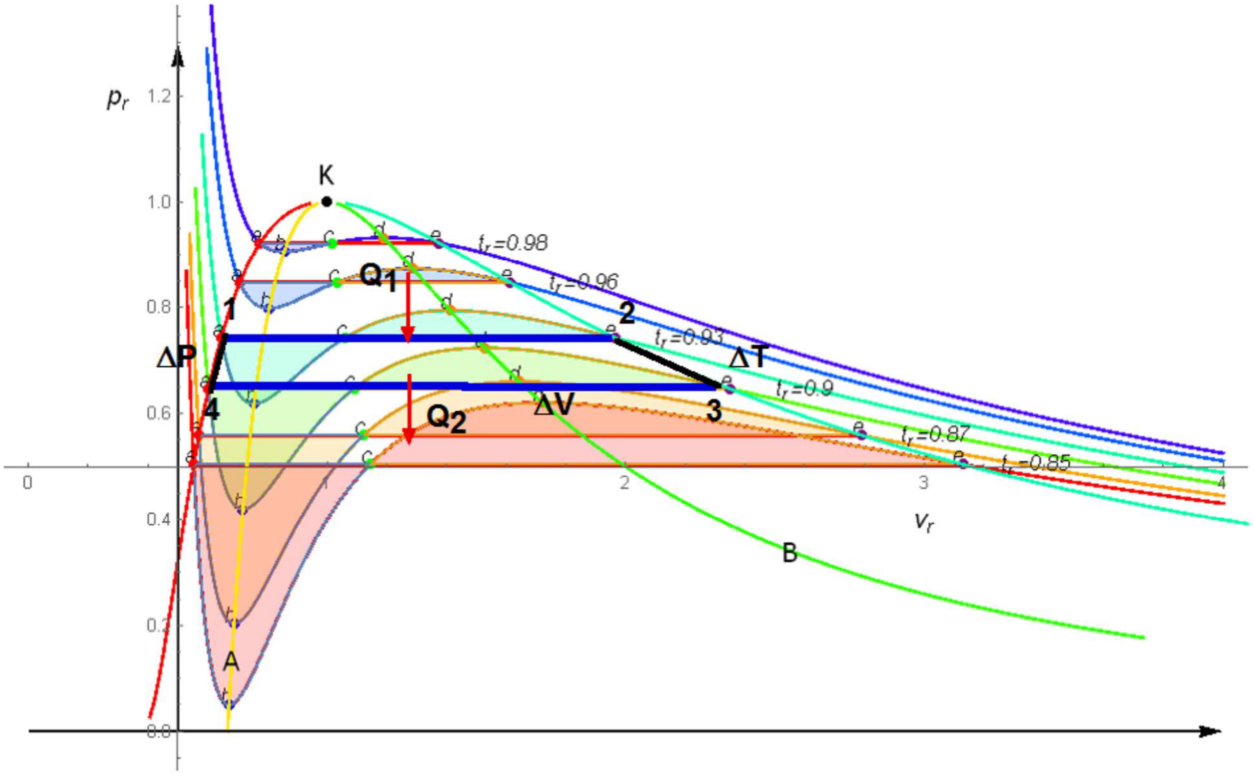


Fig. The gas-liquid co-existence in the *P* vs *V* curve for the van der Waals gas.

Carnot cycle

Path 1→2: isothermal process at the temperature $T_1 = T + \Delta T$

Path 2→3: isentropic process

Path 3→4: isothermal process at the temperature $T_2 = T$

Path 4→1: isentropic process

The work done by the system is

$$W = \Delta P \Delta V$$

where ΔV is the volume difference between the points 3 and 4, and the work corresponds to the area of closed rectangle path (1→2→3→4→1). The efficiency of the Carnot cycle is given by

$$\varepsilon = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

Thus we have

$$\varepsilon = \frac{\Delta P \Delta V}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

or

$$\frac{\Delta P \Delta V}{L} = \frac{T_1 - T_2}{T_1} = \frac{\Delta T}{T_1}$$

where $Q_1 = L$ (the latent heat)

Then we get the Clausius-Clapeyron equation;

$$\frac{\Delta P}{\Delta T} = \frac{dP}{dT} = \frac{L}{T \Delta V}.$$

3. Thermal equilibrium: chemical potential

Thermodynamic conditions for the co-existence of two phases are the conditions for the equilibrium of two systems that are in thermal, diffusive and mechanical contact.

$$T_1 = T_2$$

$$\mu_1 = \mu_2$$

$$P_1 = P_2$$

For liquid and gas

$$T_l = T_g = T, \qquad \mu_l = \mu_g, \qquad P_l = P_g = P.$$

The chemical potential:

$$\mu_l(P,T) = \mu_g(P,T)$$

At a general point in the *P*-*T* plane the two phases do not co-exist.
If $\mu_l < \mu_g$, the liquid phase alone is stable.
If $\mu_g < \mu_l$, the gas phase alone is stable.

((**Note**)) Metastable phases may occur, by supercooling or superheating.

4. Derivative of the co-existence curve, *P* vs *T*:

$$\mu_g(P_0,T_0) = \mu_l(P_0,T_0)$$

This is a condition of co-existence. We start with an equation

$$\mu_g(P_0 + dP, T_0 + dT) = \mu_l(P_0 + dP, T_0 + dT)$$

We make a series expansion

$$\mu_g(P_0,T_0) + \left(\frac{\partial \mu_g}{\partial P}\right)_T dP + \left(\frac{\partial \mu_g}{\partial T}\right)_P dT = \mu_l(P_0,T_0) + \left(\frac{\partial \mu_l}{\partial P}\right)_T dP + + \left(\frac{\partial \mu_l}{\partial T}\right)_P dT$$

In the limit as d*P* and d*T* approach zero,

$$\left(\frac{\partial \mu_g}{\partial P}\right)_T dP + + \left(\frac{\partial \mu_g}{\partial T}\right)_P dT = \left(\frac{\partial \mu_l}{\partial P}\right)_T dP + + \left(\frac{\partial \mu_l}{\partial T}\right)_P dT$$

This may be rearranged to give

$$\frac{dP}{dT} = \frac{\left(\frac{\partial \mu_l}{\partial T}\right)_P - \left(\frac{\partial \mu_g}{\partial T}\right)_P}{\left(\frac{\partial \mu_g}{\partial P}\right)_T - \left(\frac{\partial \mu_l}{\partial P}\right)_T}$$

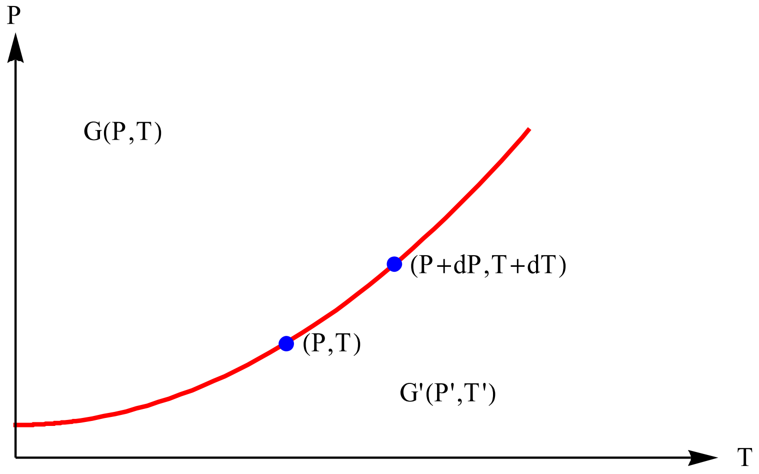


Fig. Condition for the thermal equilibrium. On the curve of co-existence, $G(P,T) = G'(P,T)$.

In the Gibbs free energy

$$G = N\mu(P,T)$$

$$dG = \mu dN - SdT + VdP$$

Thus we have

$$V = \left(\frac{\partial G}{\partial P}\right)_{N,T}, \qquad S = -\left(\frac{\partial G}{\partial T}\right)_{N,P}$$

Since $G = N\mu(P,T)$, we have

$$\left(\frac{\partial \mu}{\partial P}\right)_{N,T} = \frac{V}{N} = v, \qquad \left(\frac{\partial \mu}{\partial T}\right)_{N,P} = -\frac{S}{N} = -s$$

where v is the volume per molecule and s is the entropy per molecule. Then we have

$$\frac{dP}{dT} = \frac{s_g - s_l}{v_g - v_l}$$

5. Derivation of Clausius-Clapeyron equation from Gibbs-Duhem relation

The Gibbs energy:

$$dG = \mu dN - SdT + VdP$$

Since $G = \mu N$, this equation can be rewritten as

$$dG = \mu dN + Nd\mu = \mu dN - SdT + VdP$$

or

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP = -sdT + vdP \qquad \text{(Gibbs-Duhem relation)}$$

where $s = \frac{S}{N}$, $v = \frac{V}{N}$.

Suppose that two phases 1 and 2 are in-contact and at equilibrium with each other. The chemical potentials are related by

$$\mu_1 = \mu_2 .$$

Furthermore, along the co-existence curve,

$$d\mu_1 = d\mu_2$$

Here we use the Gibbs-Duhem relation,

$$d\mu = -sdT + vdP$$

to obtain

$$-s_1 dT + v_1 dP = -s_2 dT + v_2 dP$$

or

$$\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1}$$ (Clausius-Clapeyron equation)

6. Clausius-Clapeyron equation

$$d'Q = T(s_g - s_l) = l$$

l: latent heat of vaporization/molecule

$$\Delta v = v_g - v_l$$

Thus we have the Clausius-Clapeyron equation,

$$\frac{dP}{dT} = \frac{l}{T\Delta v}$$

Two approximations:

(a) $v_g >> v_l$

$$\Delta v = v_g - v_l \approx v_g = \frac{V_g}{N_g}$$

(b)

$$PV_g = N_g k_B T$$ (ideal gas law)

or

$$Pv_g = k_B T$$

Using these two approximations, we have

$$\frac{dP}{dT} = \frac{l}{T\Delta v} = \frac{l}{Tv_g} = \frac{lP}{TPv_g} = \frac{lP}{k_B T^2}$$

Suppose that the latent heat l is independent of T;

$$\int \frac{dP}{P} = \frac{l}{k_B} \int \frac{dT}{T^2}$$

or

$$\ln P = -\frac{l}{k_B T} + \text{constant}$$

or

$$P(T) = P_0 \exp(-\frac{l}{k_B T})$$

where L_0 is the latent heat of vaporization of one molecule. If L_0 refers instead to one mole, then

$$\frac{l N_A}{k_B N_A} = \frac{L}{R}$$

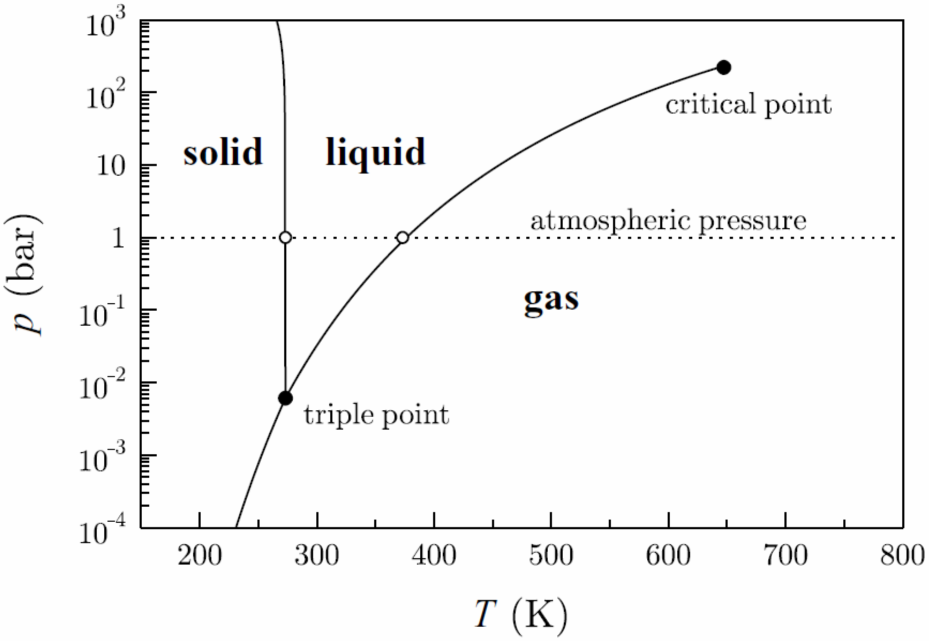
$$P(T) = P_0 \exp(-\frac{L}{RT}).$$

where

R = 8.3144598 [J/(K mol)]. $L = l N_A$.

L = 2256 x 18.01528 = 40.642 (kJ/mol): latent heat of vaporization/mol for water:

7. Phase diagram of H_2O and Clausius-Clapeyron equation



solid
liquid
gas
critical point
atmospheric pressure
triple point
10^3
10^2
10
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
p (bar)
200
300
400
500
600
700
800
T (K)

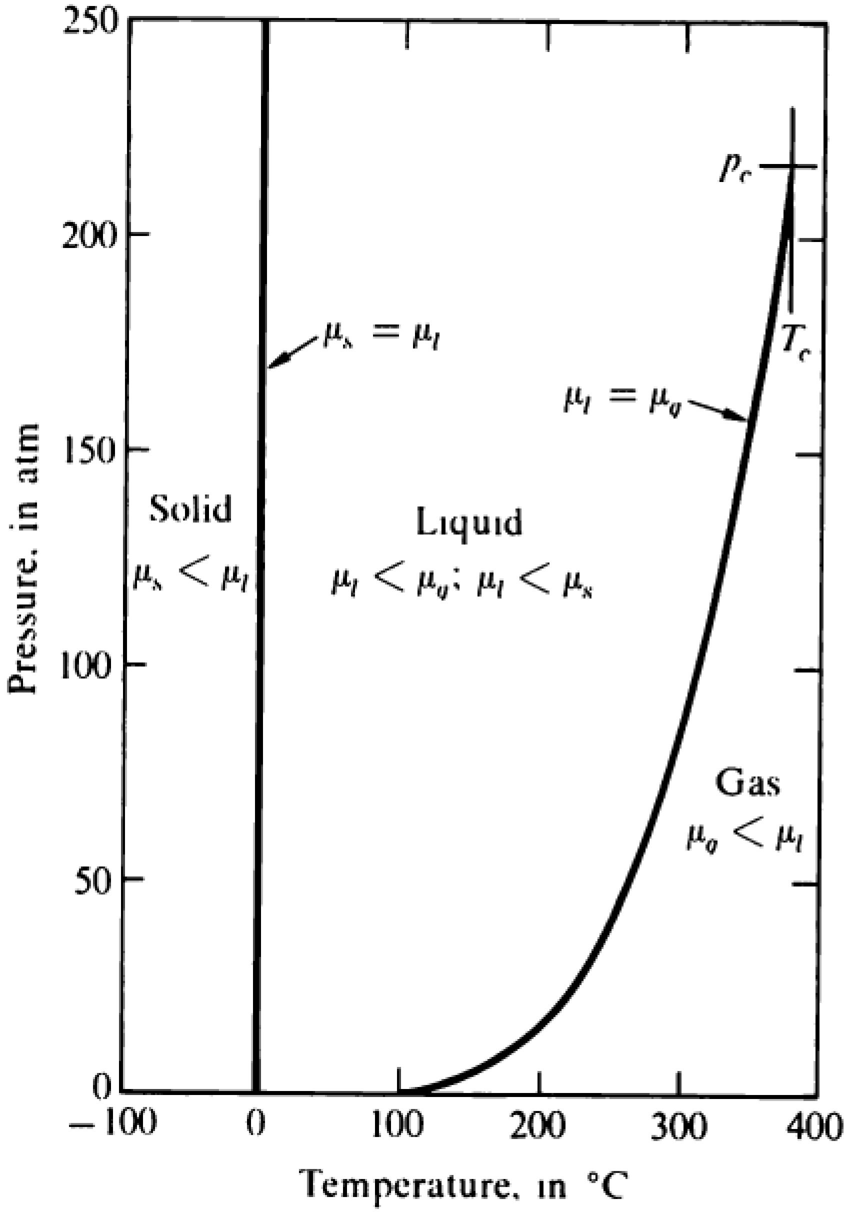


Fig. Phase diagram of H_2O. The relationships of the chemical potentials μ_s, μ_l, and μ_g in the solid, liquid, and gas phases are shown. The phase boundary here between ice and water is not exactly vertical: the slope is actually negative, although very large. (Kittel, Thermal Physics).

For the transition between vapor (gas) and water (liquid), experimentally we have

$$\frac{dP}{dT} = \frac{s_g - s_l}{v_g - v_l} > 0 \qquad \text{(see the phase diagram of water)}$$

Since $v_g > v_l$, we get

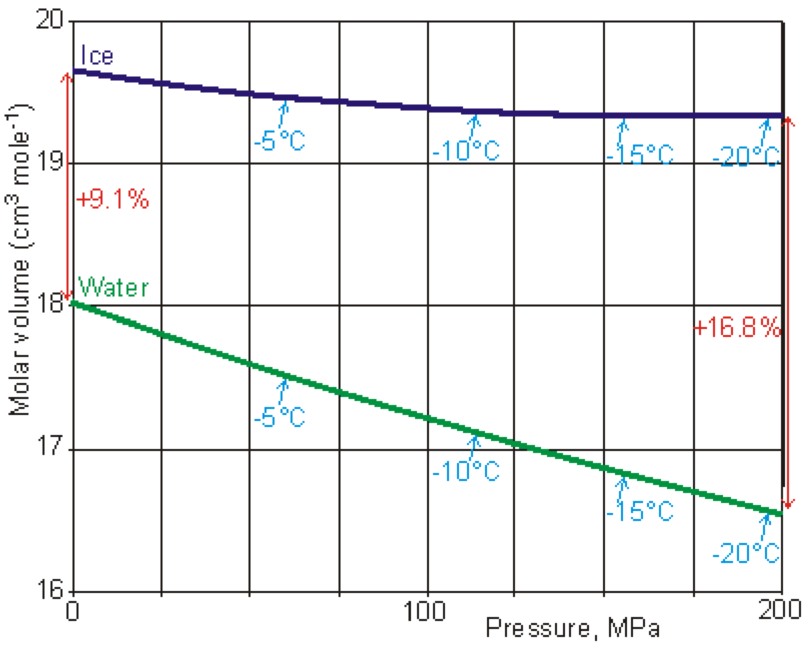
$$s_g > s_l$$

For the transition between ice (solid) and water (liquid), experimentally we have

$$\frac{dP}{dT} = \frac{s_s - s_l}{v_s - v_l} < 0 \qquad \text{(see the phase diagram of water)}$$

((**Note**)) $v_s > v_l$ for water

The liquid state of a substance occupies more volume than the solid state for same substance with the same mass. A notable exception to this rule is water, which is actually less dense in its solid form than its liquid form (this is why ice floats in water). This is due to the hydrogen bonding that occurs between molecules of H_2O. Because the hydrogen bonds formed in water are perfectly structured (just the right number of oxygen atoms to interact with the hydrogen atoms), as a solid water forms a lattice structure that spaces out the molecules more than they would be in liquid form.



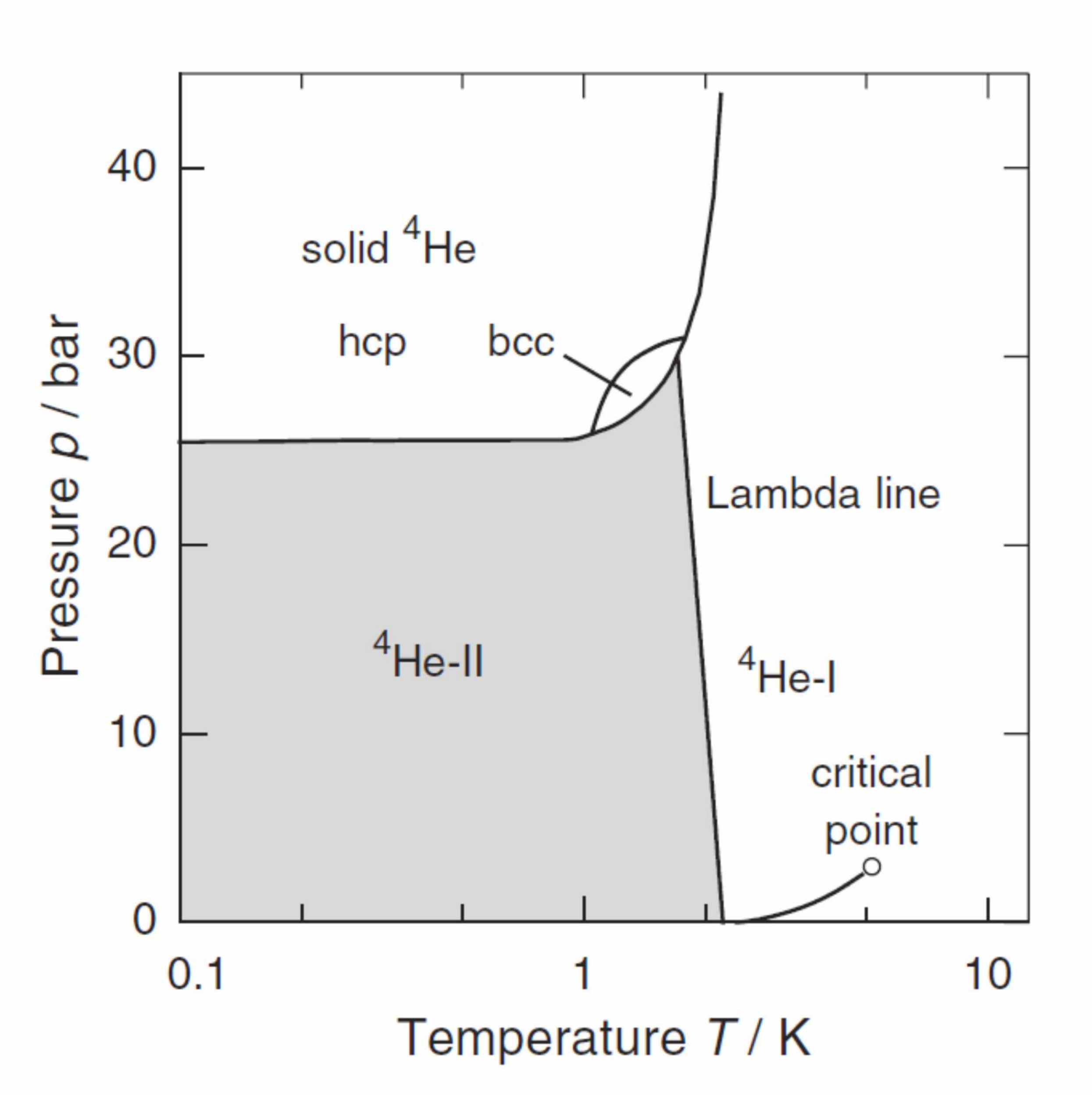
Since $v_s > v_l$, we get

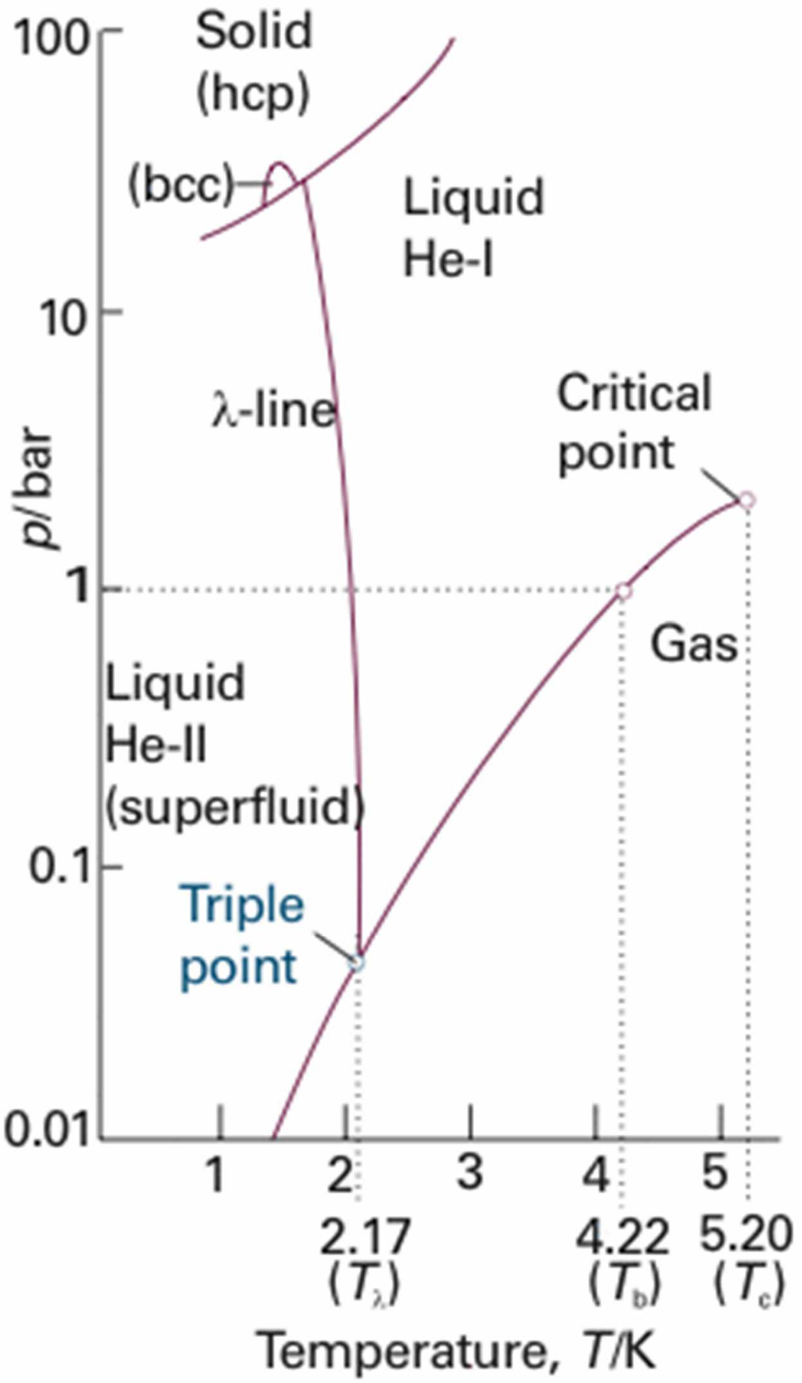
$s_l > s_s$

In summary, we have

$s_g > s_l > s_s$

8. Phase diagram of liquid ^{4}He




Solid
(hcp)
(bcc)
Liquid
He-I
λ-line
Critical
point
Gas
Liquid
He-II
(superfluid)
Triple
point
p/bar
100
10
1
0.1
0.01
1
2
3
4
5
2.17
(T_λ)
4.22
(T_b)
5.20
(T_c)
Temperature, T/K

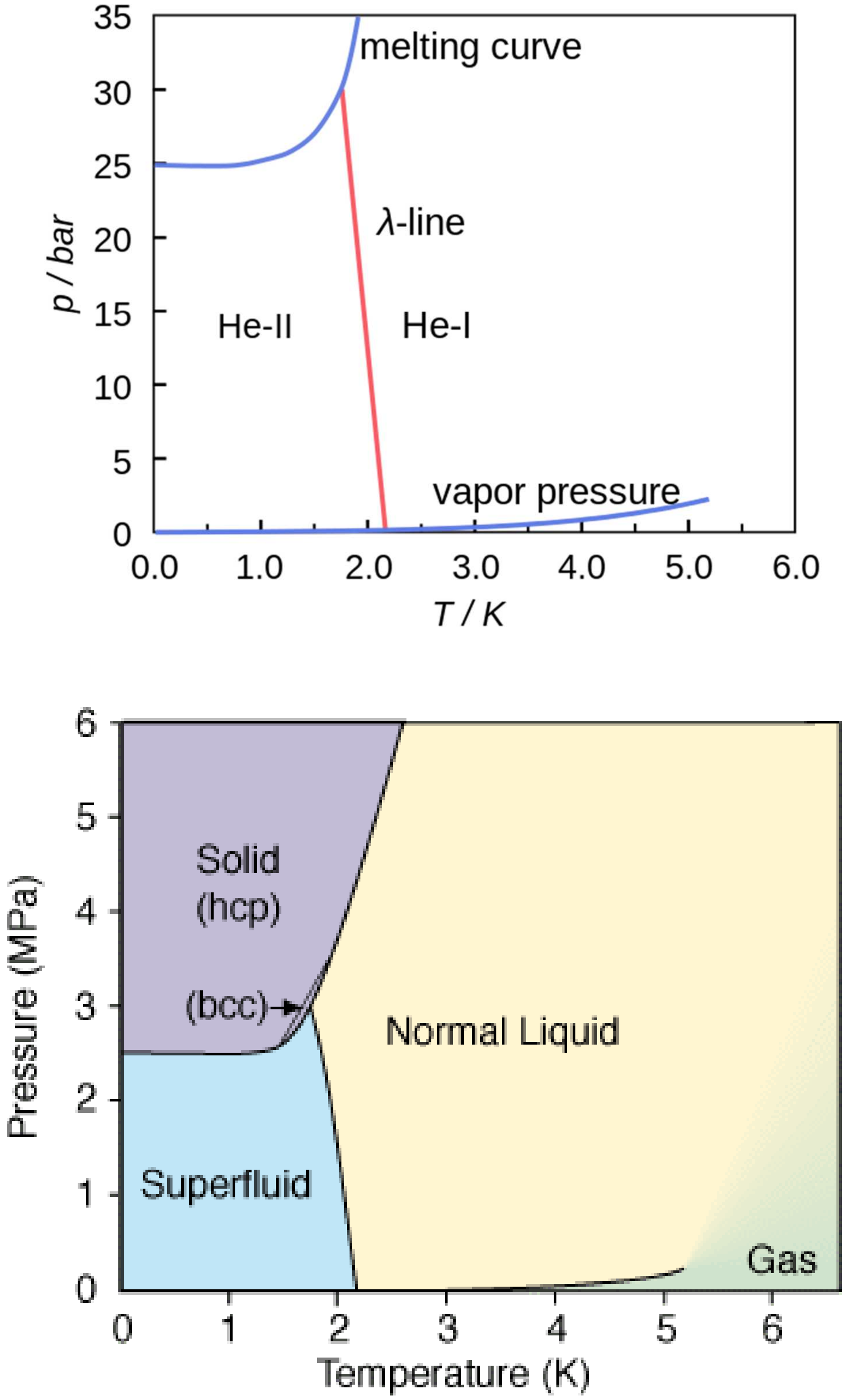


Fig. Phase diagram of ^{4}He.

The Clausius-Clayperon equation is also applied to the solid-liquid transition

$$\frac{dP}{dT} = \frac{s_l - s_s}{v_l - v_s}$$

In the phase diagram of ^{4}He, the liquid-solid co-existence curve is closely horizontal for T<1.4 K.

$$\Rightarrow \qquad s_l \approx s_s$$

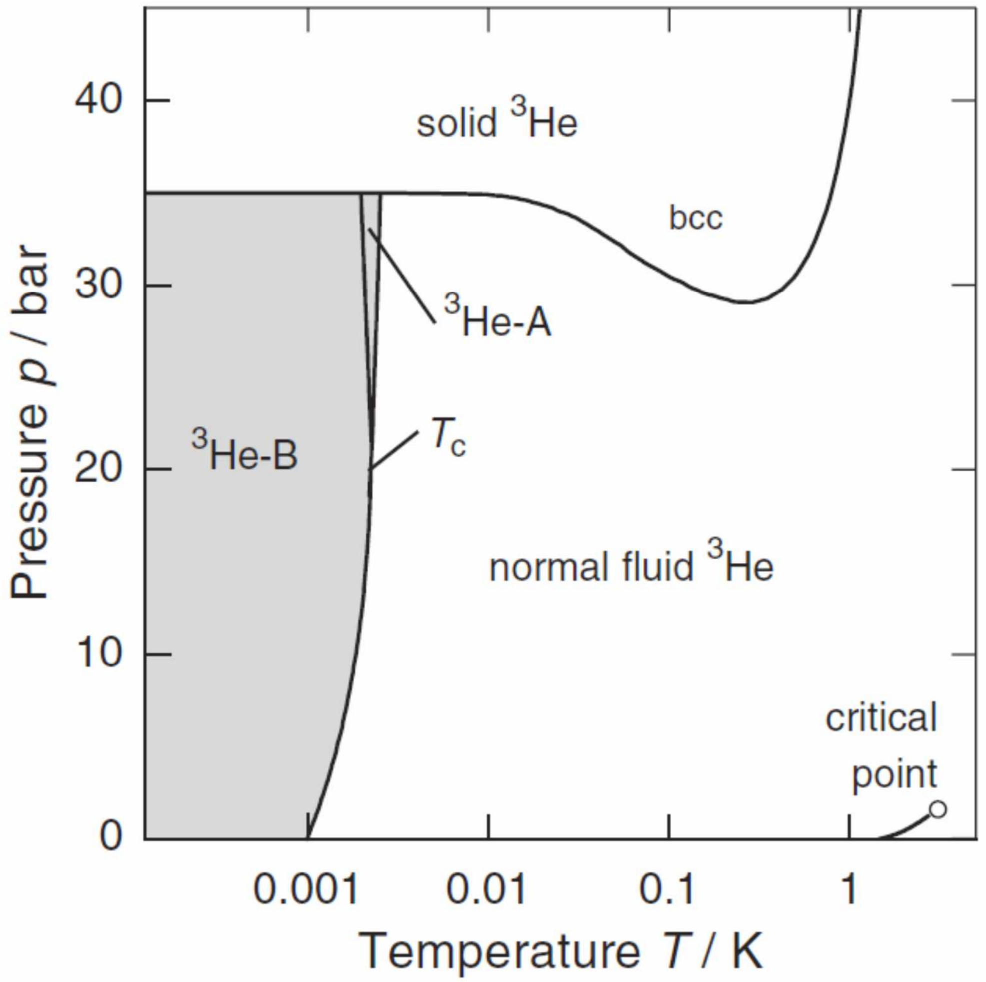
Note that the entropy of a normal liquid is considerably higher than that of a normal solid.

At low temperatures ($T \approx 0.8$ K) the melting curve exhibits a shallow minimum, which is not deep enough to be visible on the scale of the phase diagram of ^{4}He,. Using the Clausius Clapeyron equation curve, we can draw conclusions about the entropies of liquid and solid ^{4}He. Since $v_s < v_l$, we have

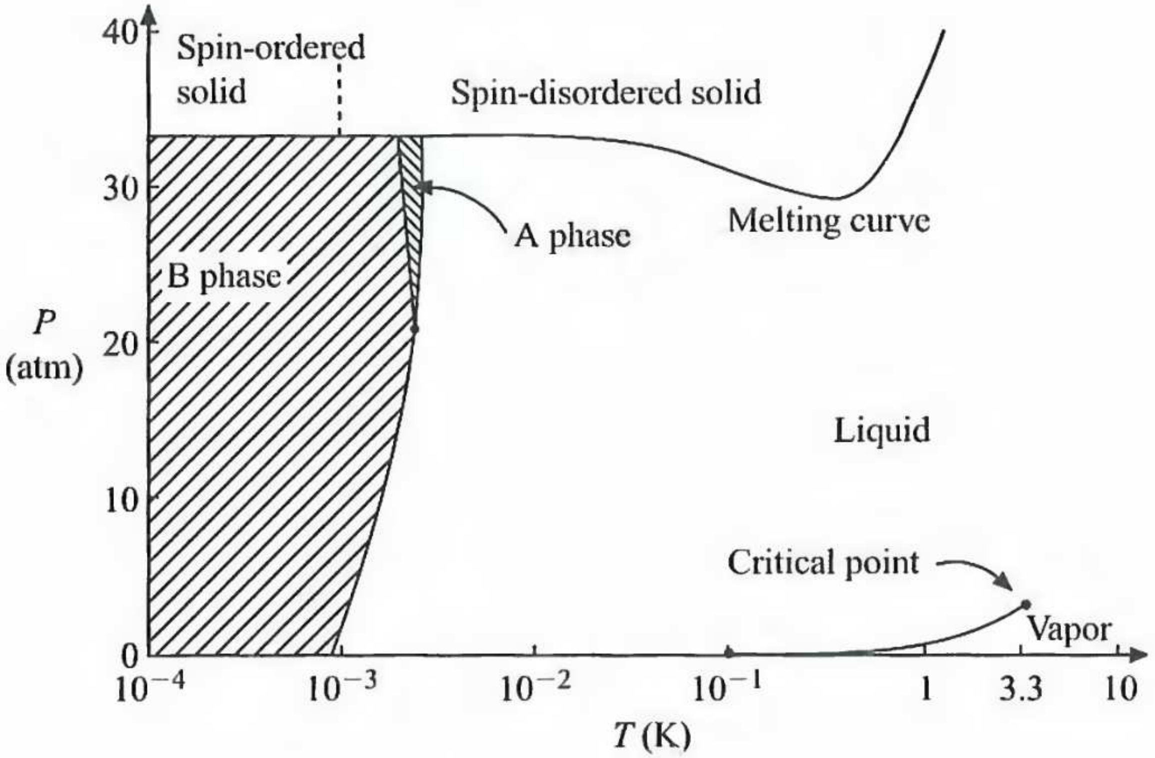
$$s_l < s_s$$

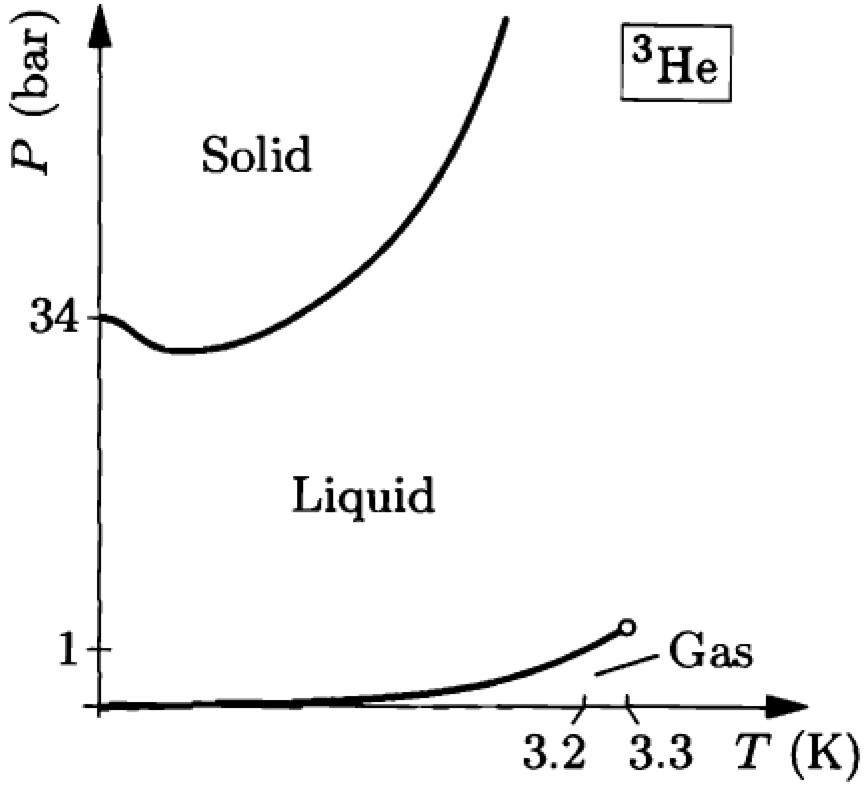
which means that the entropy of the solid phase is larger than the entropy of the liquid phase. In other words, the disorder in the solid is larger than in the liquid. The entropy of solid and liquid ^{4}He is determined by thermal excitations in this temperature range. It turns out that solid ^{4}He has a slightly higher phonon heat capacity than liquid ^{4}He, because of the low transverse sound velocity in solid ^{4}He. Therefore, at low temperatures the entropy of solid ^{4}He is larger than that of liquid ^{4}He.

9. Phase diagram of liquid ^{3}He



solid ^{3}He
bcc
^{3}He-A
^{3}He-B
T_c
normal fluid ^{3}He
critical point
40
30
20
10
0
0.001
0.01
0.1
1
Pressure p / bar
Temperature T / K


40
30
20
10
0
P
(atm)
Spin-ordered solid
Spin-disordered solid
A phase
B phase
Melting curve
Liquid
Critical point
Vapor
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1
3.3
10
T (K)


P (bar)
³He
Solid
34
Liquid
1
Gas
3.2
3.3
T (K)

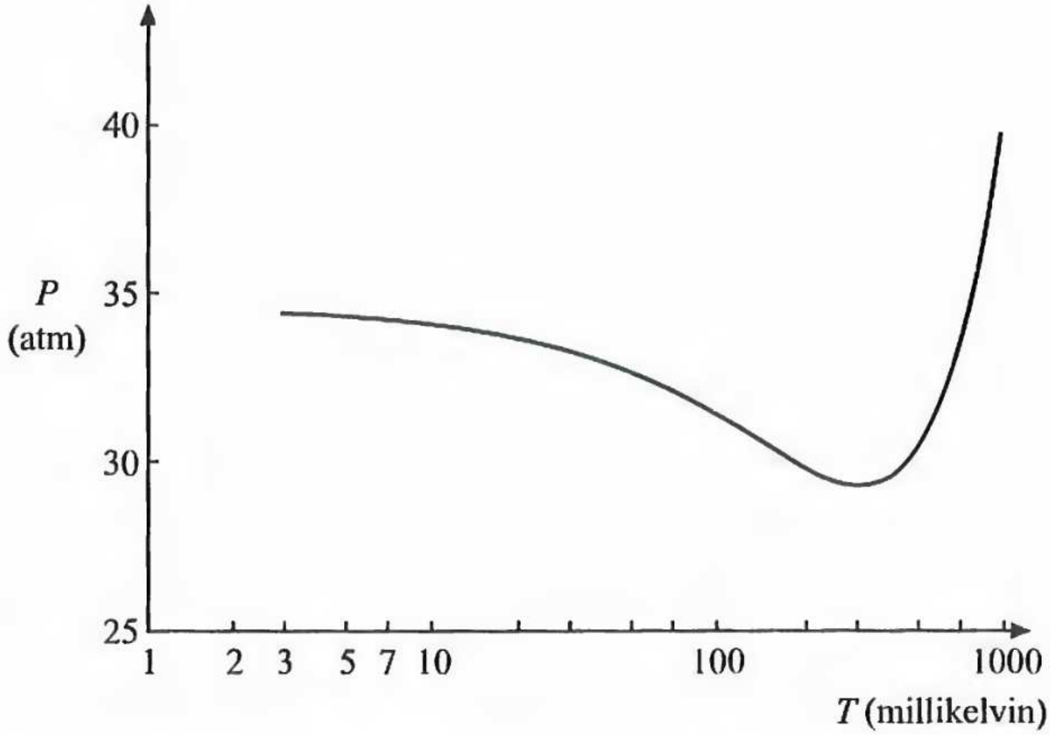


Fig. Phase diagram of ^{3}He.

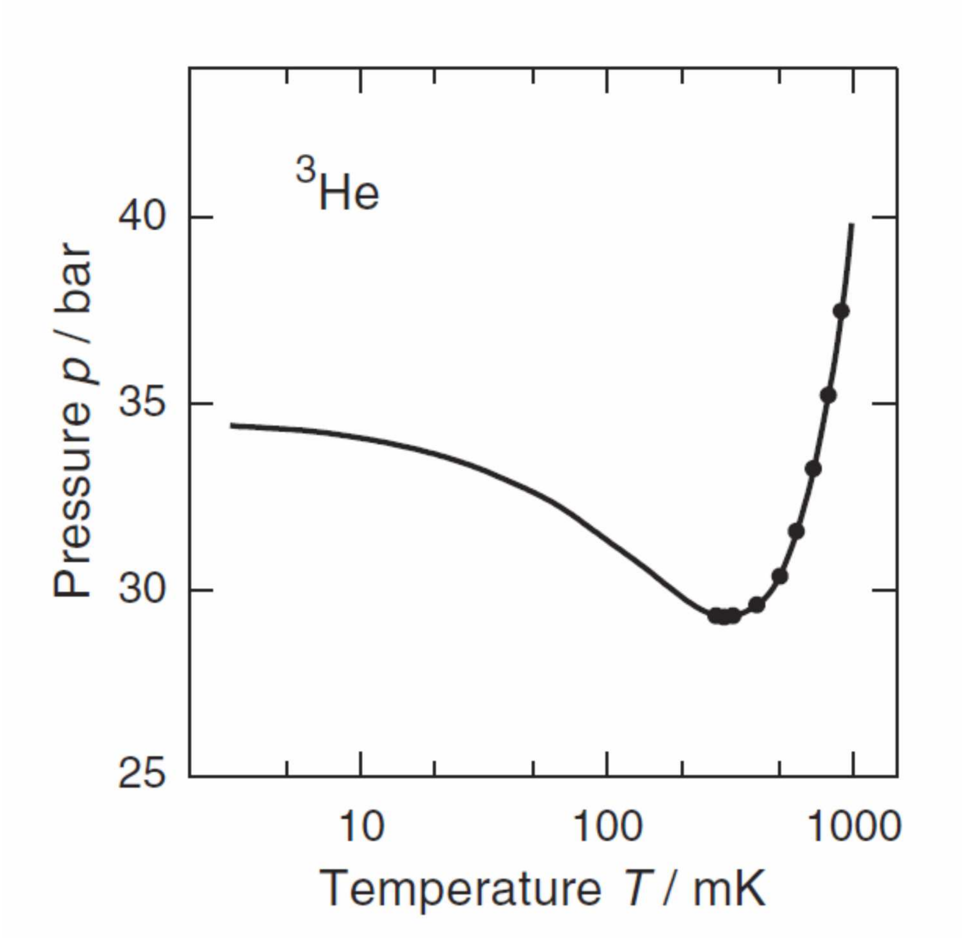


Fig. Phase diagram of ^{3}He.

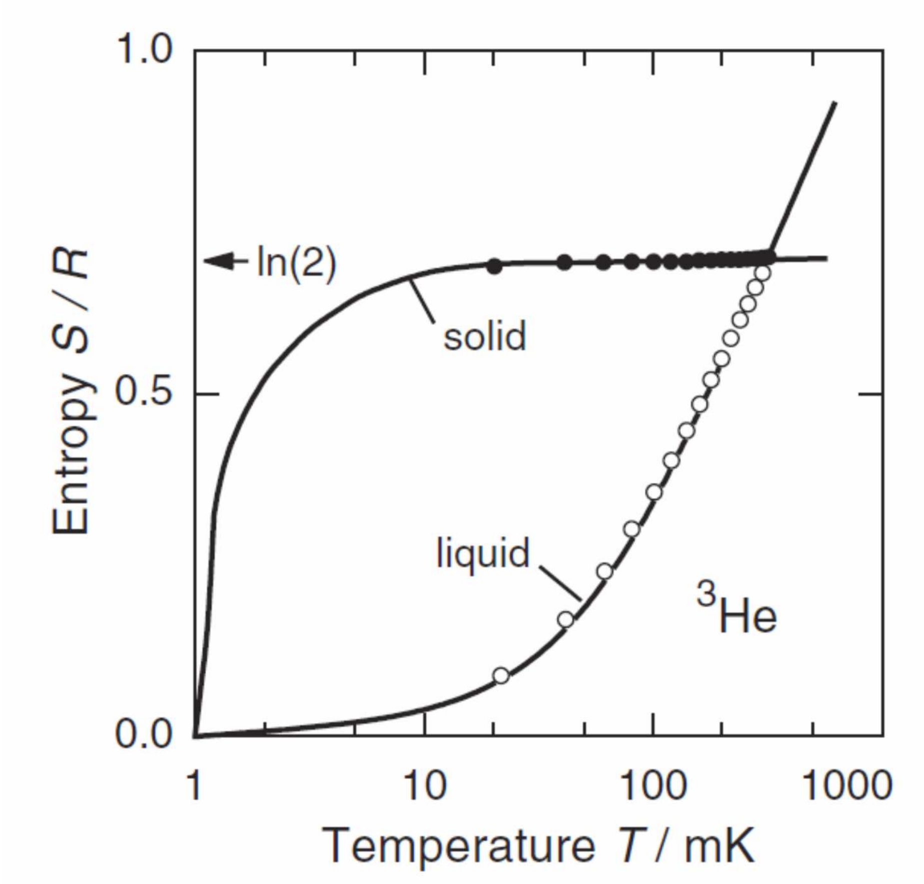
The Clausius-Clapeyron equation,

$$\frac{dP}{dT} = \frac{s_l - s_s}{v_l - v_s} < 0$$

Since $v_l > v_s$, we have

$$s_l < s_s.$$

The entropy of liquid is less than the entropy of the solid.



The solid has more accessible states than liquid. Liquid ^{3}He has a relatively low entropy for a liquid because it approximates a Fermi gas, which generally has a low entropy when $T << T_F$, because a large portion of the atoms have their momenta ordered into the Fermi sphere.

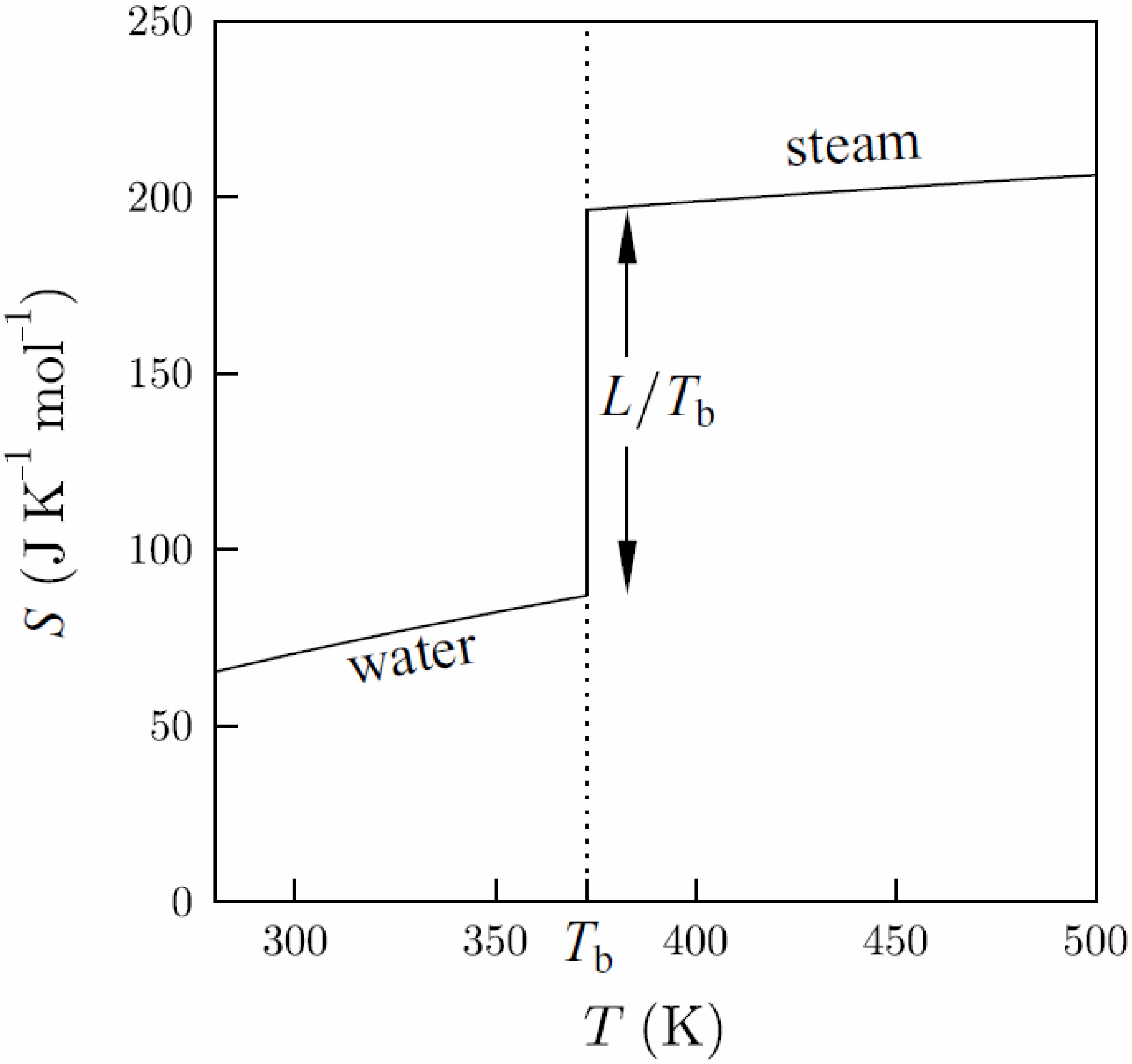
The Grand potential:

$$\Phi_G = -\frac{2N}{5}\varepsilon_F(1+\frac{5}{8}\pi^2\frac{{k_B}^2T^2}{{\varepsilon_F}^2})$$

The entropy:

$$
\begin{aligned}
S &= -\left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\mu} \\
&= \frac{2N}{5}\varepsilon_F\left(\frac{5}{8}\pi^2\frac{{k_B}^2}{{\varepsilon_F}^2}\right)2T \\
&= Nk_B\left(\frac{\pi^2 k_B T}{2\varepsilon_F}\right) \\
&= Nk_B\frac{\pi^2}{2}\left(\frac{T}{T_F}\right)
\end{aligned}
$$

10. Latent heat and enthalpy



When we cross the co-existence curve ($\mu_g = \mu_l$)

$$
\begin{aligned}
L &= T\Delta S \\
&= \Delta E + P\Delta V - (\mu_g - \mu_l)\Delta N \\
&= \Delta E + P\Delta V
\end{aligned}
$$

The enthalpy H is defined by

$$H = E + PV$$

$$dH = dE + PdV + VdP$$

At constant pressure ($dP = 0$)

$$L = T\Delta S = \Delta E + P\Delta V = \Delta H = H_g - H_l$$

Values of H are tabulated,

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$$H = \int C_P dT$$

11. Example-1 (Kittel 10-3)

Calculation of $dT/.dP$

Calculate from the vapor pressure equation the value of d*T*/d*P* near *P* = 1 atm for the liquid-vapor equilibrium of water. The heat of vaporization at 100 C is 2260 J/g. Expain the result in K/atm.

((**Solution**))

Clausius-Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \approx \frac{L}{TV_g} = \frac{PL}{T(PV_g)} = \frac{PL}{RT^2}$$

where *R* is the gas constant,

R=8.3144598 J/(mol K) = 1.9872036 cal/(mol K)

L is the latent heat of vaporization /mol.

$L = 2264.705 J/g = 9743.005 cal/mol =$ 40764.7 J/mol

For *T* = 373 K and *P* = 1 atm, we get

$$\frac{dP}{dT} = \frac{PL}{RT^2} = 0.0352397\,(atm/K)$$

or

$$\frac{dT}{dP} = 28.3771 \text{ K/atm.}$$

12. Example-2 (Kittel 10-3)

Heat of vaporization of ice

The pressure of water vapor over ice is 3.88 mmHg at -2 C and 4.58 mmHg at 0 C. Estimate in J/mol the heat of vaporization of ice at -1 C.

((**Solution**))

Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \approx \frac{L}{TV_g} = \frac{PL}{T(PV_g)} = \frac{PL}{RT^2}$$

leading to

$$\ln P = -\frac{L}{RT} + \text{const} \qquad (1)$$

For the two points (P_1, T_1) and (P_{21}, T_2) on the curve given by Eq.(1),

$$\ln\left(\frac{P_1}{P_2}\right) = -\frac{L}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

or

$$\frac{L}{R} = \frac{\ln\left(\frac{P_1}{P_2}\right)}{\left(\frac{1}{T_2} - \frac{1}{T_2}\right)} = 6135.55$$

or

$$L = 51013.9 \text{J/mol}$$

13 Example 3 (Huang problem 4-5)

Clausius-Clapeyron on liquid ^{3}He

(a) In a liquid-[gas transition, the specific volume of the liquid (phase 1) is usually negligible compared with that of the gas (phase 2), which usually can be treated as an ideal gas. let $l = T(s_2 - s_1)$ be the latent heat of evaporation per particle. Under the approximation mentioned, show that

$$\frac{T}{P}\frac{dP}{dT} = \frac{l}{k_B T}$$

(b) Use this formula to obtain the latent heat per unit mass for liquid ^{3}He, in 0.2 K increments of *T*, from the following table of vapor pressures of ^{3}He. The mass of a ^{3}He is

$$m = 3.0160293u = 5.007 \times 10^{-24}\ g\,.$$

T(K)	*P*(microns of Hg)
0.200	0.0121
0.201	0.0130
0.400	28.12
0.401	28.71
0.600	544.5
0.601	550.3
0.800	2892
0.801	2912
1.000	8842
1.005	9053
1.200	20163
1.205	20529

((**Solution**))

Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l} \approx \frac{\Delta S}{V_g}$$

Equation of state for the ideal gas:

$$PV_g = Nk_B T$$

Thus we get

$$\frac{dP}{dT} = \frac{P\Delta S}{PV_g} = \frac{P\Delta S}{Nk_B T}$$

or

$$\frac{T}{P}\frac{dP}{dT} = \frac{\Delta S}{Nk_B} = \frac{L}{TNk_B} = \frac{l}{k_B T}$$

or

$$\int \frac{1}{P} dP = \frac{l}{k_B} \int \frac{dT}{T^2}, \qquad \ln P = -\frac{l}{k_B T} + C$$

$$l(\text{erg/particle}) = \frac{3.060293g}{N_A} l \ \ (\text{erg/g})$$

$$\frac{l}{k_B} = \frac{3.060293\, l(\text{erg/g})}{R} = \frac{3.060293\, l(\text{erg/g})}{8.3144598} \times 10^{-7}$$

or

$$\frac{l}{k_B} = 3.68069 \times 10^{-8} l(\text{erg/g})$$

where

$$R = N_A k_B = 8.3144598 \text{ x } 10^7 \text{ erg/(K mol)}$$

$$\ln P = C - \frac{1}{T} 3.68069 \times 10^{-8} l(\text{erg/g})$$

$$\text{slope} = -\frac{d \ln P}{d(1/T)} = 3.68069 \times 10^{-8} l(\text{erg/g})$$

Fig.1 Plot of ln$P$ vs 1/T.

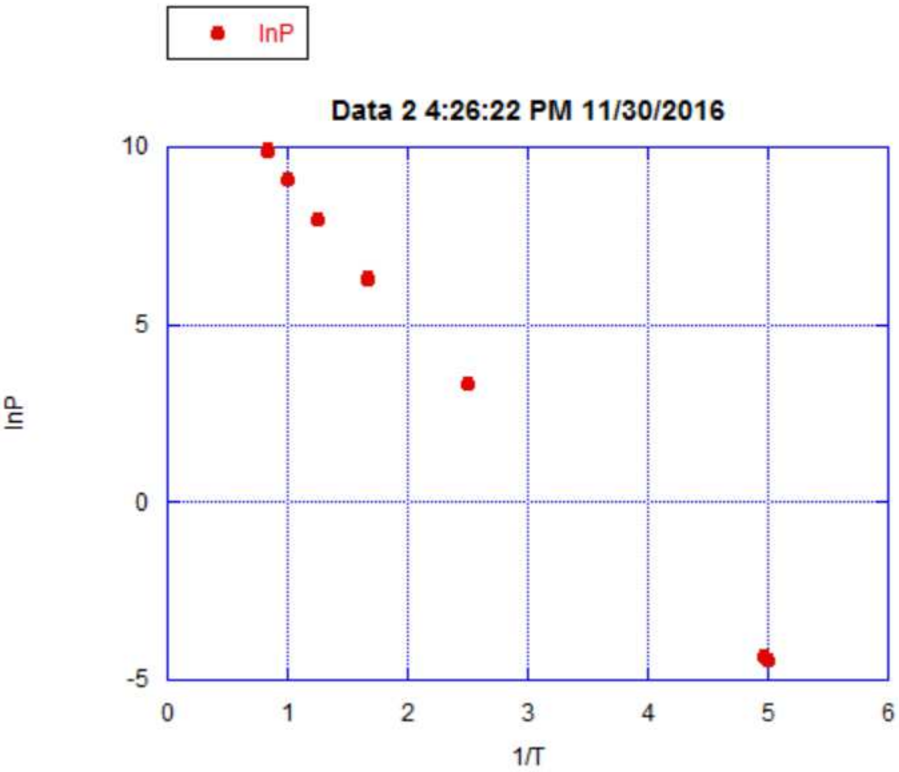
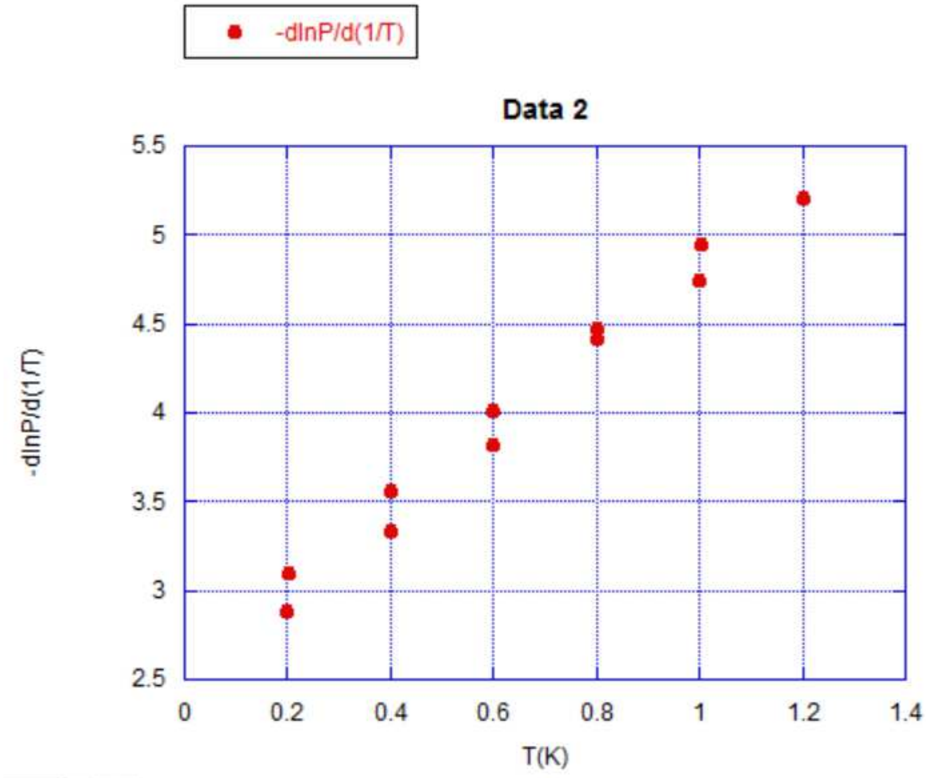


Fig.2 Plot of $-d\ln P/d(1/T)$ vs T



The latent heat can be obtained from the value of $-d\ln P/d(1/T)$ at each temperature.

$T = 0.2$ K	slope = 3.0	$l = 8.15$ x 10^7 (erg/g)
$T = 0.4$ K	slope = 3.4	$l = 9.24$ x 10^7 (erg/g)
$T = 0.6$ K	slope = 3.9	$l = 10.60$ x 10^7 (erg/g)
$T = 0.8$ K	slope = 4.4	$l = 11.95$ x 10^7 (erg/g)
$T = 1.0$ K	slope = 4.8	$l = 13.04$ x 10^7 (erg/g)
$T = 1.2$ K	slope = 5.2	$l = 14.13$ x 10^7 (erg/g)

14 Example 4 (Blundell-Blundell 28-6)

It is sometimes stated that the weight of a skater pressing down on their thin skates is enough to melt ice, so that the skater can glide around on a thin film of liquid water. Assuming an ice rink at -5° C, do some estimates and show that this mechanism will not work. (In fact, frictional heating of ice is much more important, see S.C. Colbeck, Am. J. Phys. 63, 888 (1995) and S.C. Colbeck, L. Najarian, and H.B. Smith Am. J. Phys. 65, 488 (1997).)

((**Solution**))

$\rho_l = 1.00\times 10^3$ kg/m^3, $\rho_s = 0.917\times 10^3$ kg/m^3,

$$V_l = \frac{1}{\rho_l} = 1.00 \times 10^{-3} \text{ m}^3\text{/kg}, \quad V_s = 1.091 \times 10^{-3} \text{ m}^3\text{/kg},$$

$L_f = 334$ kJ/kg (latent heat of fusion for water)

$$\frac{dP}{dT} = \frac{S_l - S_s}{V_l - V_s} = \frac{1}{T}\frac{L_f}{V_l - V_s} = -\frac{1}{273}\frac{3.34 \times 10^5}{0.091 \times 10^{-3}} = -1.34 \times 10^7 \text{ Pa/K} = \text{-132.2 atm/K.}$$

where

1 atm = 1.01315 x 10^5 Pa.

For a very heavy skater (100 kg), only making the contact with ice over an area 10 cm x 1 mm = 10^{-4} m^2.

$$\Delta P = \frac{100 \times 9.8}{10^{-4}} = 9.8 \text{ x } 10^6 \text{ Pa} = 96.7 \text{ atm}$$

Then

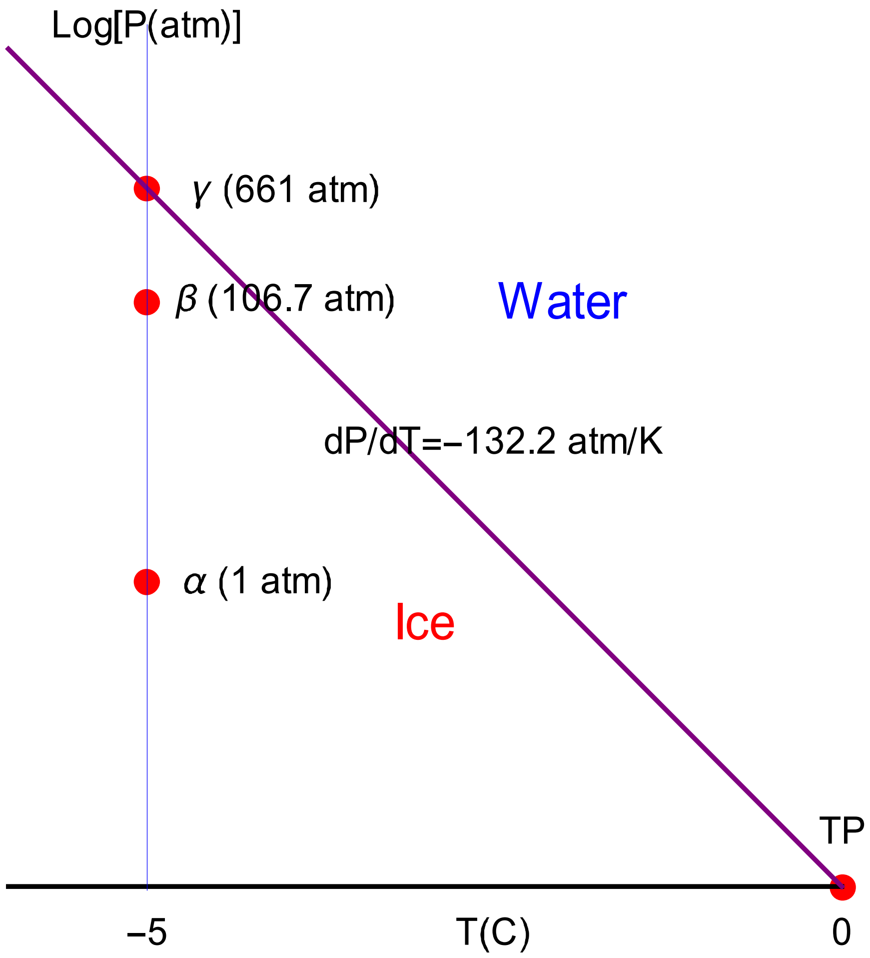


Fig. TP (triple point): $T = 0$ C (273.16 K) and $P = 0.00637$ atm. The stating point α: $T = -5$ C and $P = 1$ atm.

We now suppose that the temperature is -5 C. At 1 atmosphere, the ice is in the state α on the P-T plane. There is no water present. When the ice skater puts pressure on the ice, the state moves along the constant temperature line ($\alpha - \beta - \gamma$). In theory, as soon as the phase boundary is reached at the state γ, some ice melts so that the edge of the skate sinks in fractionally, with the load now spread over a large area stabilizing the pressure. The state thus remains fixed at γ, with the liberated water acting as a lubricant.

The question must be asked: Is 106.7 atm or so sufficient to achieve this goal? From

$$\frac{dP}{dT} = \text{-132.2 atm/K}.$$

So a pressure increase of (132.2 atm/K) x 5 K = 661 atm would be required to go to from α to γ. Thus this explanation for the success of the skater appears inadequate.

((**Note**))

Thermal conductivity:

$$\kappa_{ice} = 2.3 \text{ W/(m K)}$$

$$\kappa_{water} = 0.56 \text{ W/(m K)}$$

The gas constant:

$$R = 8.3145 \text{ J/(K mol)}$$

Latent heat of fusion:

$$L_f = 334 \text{ kJ/kg}$$

Latent heat of vaporization:

$$L_v = 2260 \text{ kJ/ kg}$$

The density

$$\rho_{water} = 1.00 \times 10^3 \text{kg/m}^3.$$

$$\rho_{ice} = 0.917 \times 10^3 \text{kg/m}^3.$$

$$\frac{1}{\rho_{ice}} - \frac{1}{\rho_{water}} = 0.0951 \times 10^{-3} \text{ m}^3\text{/kg}$$

REFERENCES

C. Kittel and H. Kroemer, Thermal Physics, second edition (W.H. Freeman and Company, 1980).
C.J. Adkins, An Introduction to Thermal Physics (Cambridge 1987).
C.J. Adkins, Equilibrium Thermodynamics, third edition (Cambridge, 1983).
K. Huang, Introduction to Statistical Physics, second edition (CRC Press, 2010).

APPENDIX-1

Derivation of Clausius-Clapeyron equation from the Maxwell's relation.

Using the Maxwell's relation we have

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

which leads to the Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V}.$$

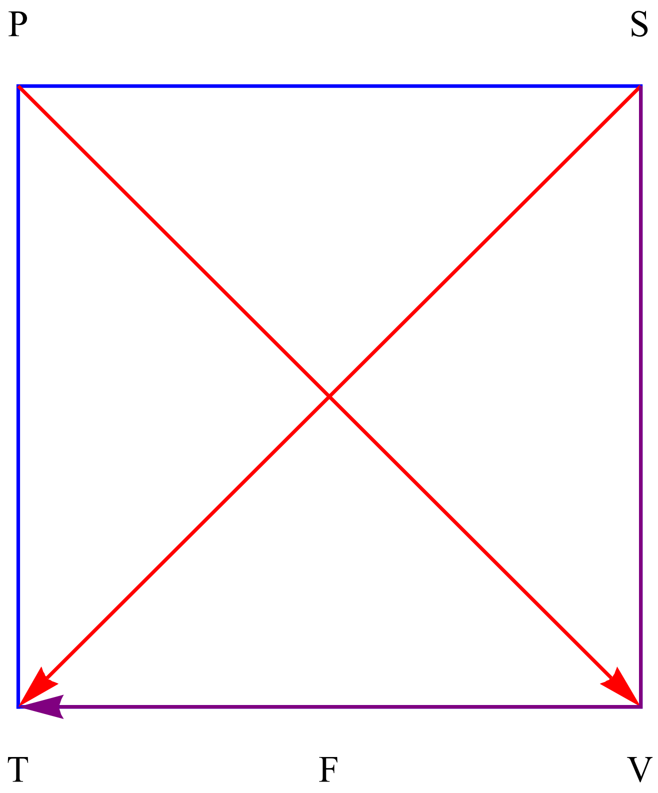
APPENDIX-II

Maxwell relation

(ii) Maxwell's relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

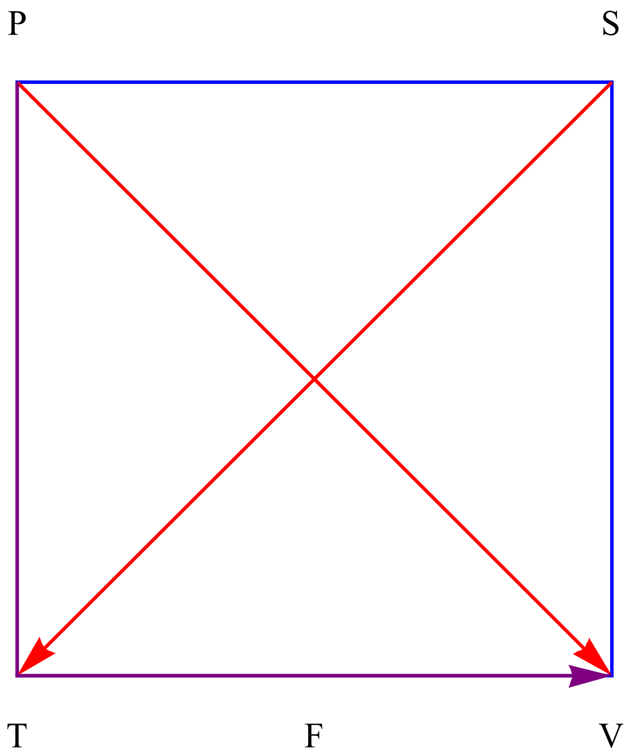
Here we consider the Maxwell's relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

For $\left(\frac{\partial S}{\partial V}\right)_T$, in the Born diagram, we draw the lines along the vectors $\overrightarrow{SV}$ and $\overrightarrow{VT}$. The resulting vector is $\overrightarrow{ST} = \overrightarrow{SV} + \overrightarrow{VT}$ (the direction of sun light)



For $\left(\frac{\partial P}{\partial T}\right)_V$, in the Born diagram, we draw the lines along the vectors $\overrightarrow{PT}$ and $\overrightarrow{TV}$. The resulting vector is $\overrightarrow{PV} = \overrightarrow{PT} + \overrightarrow{TV}$ (the direction of water flow). Then we have the positive sign in front of $\left(\frac{\partial P}{\partial T}\right)_V$ such that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$


P
S
T
F
V