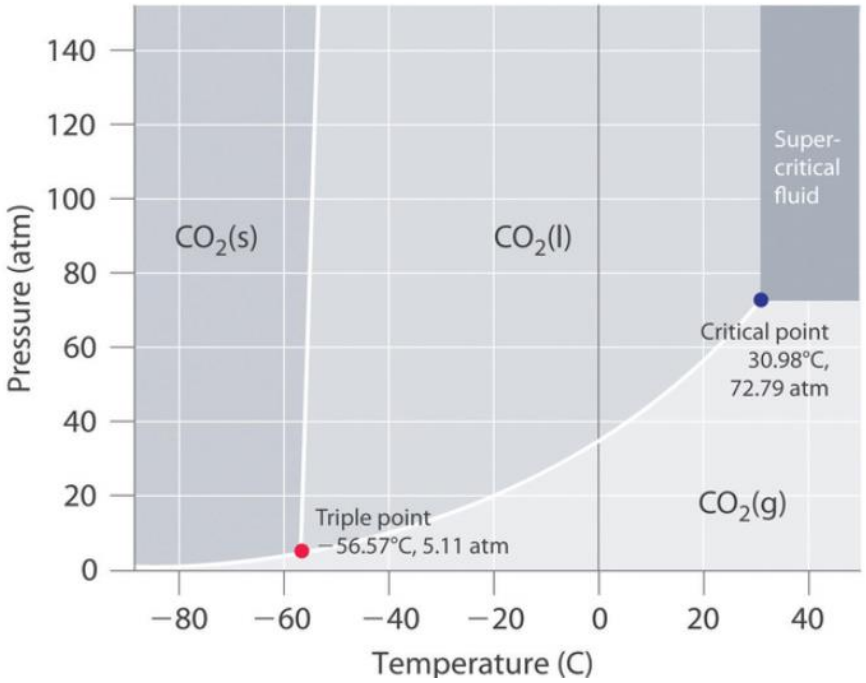
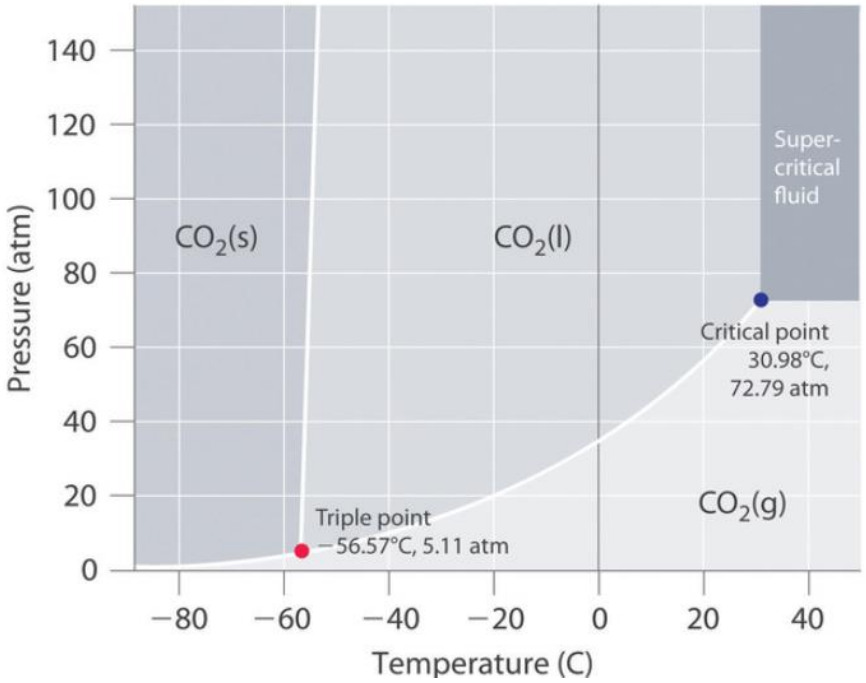
Phase diagram – CO_2

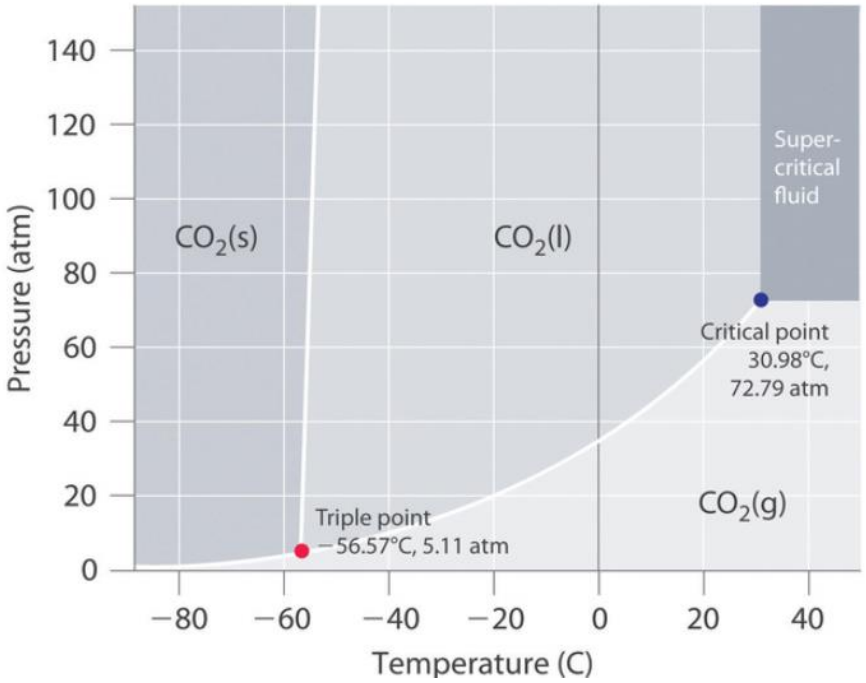


Phase diagram – CO_2



- The phase diagram shows the regions of P and T at which phases are thermodynamically stable. A single phase is represented by a certain area.

Phase diagram – CO_2



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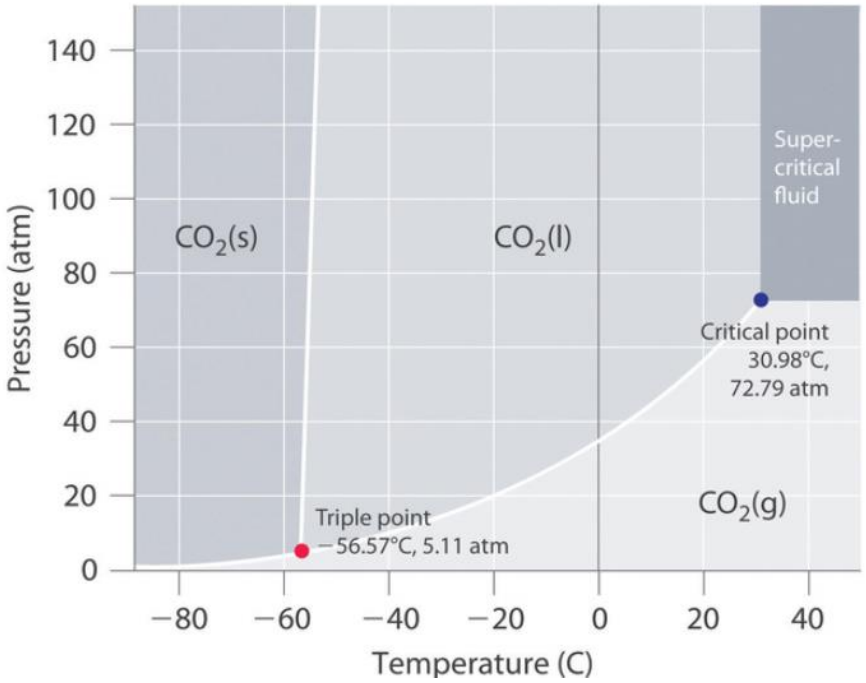
Phase diagram – CO_2



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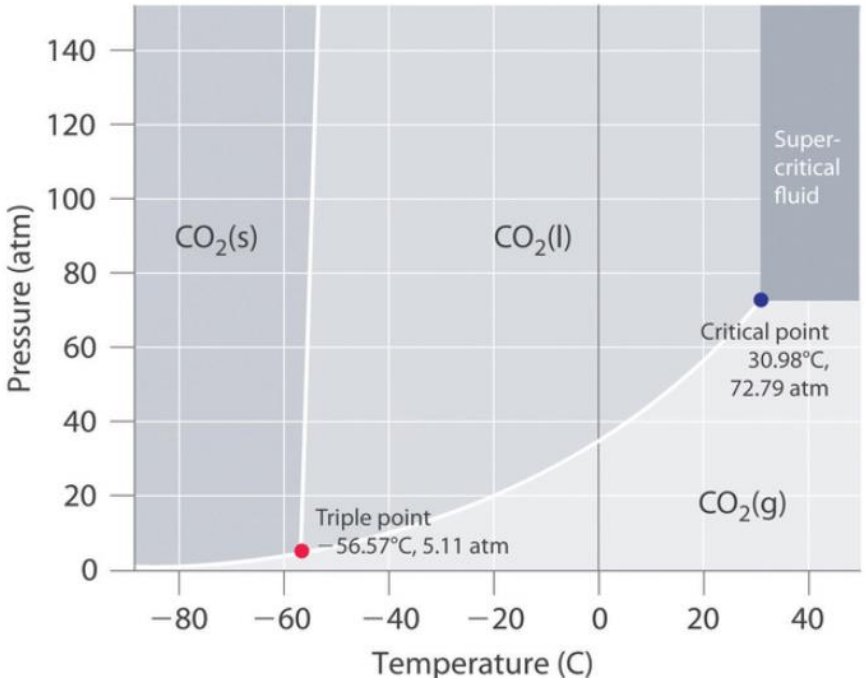

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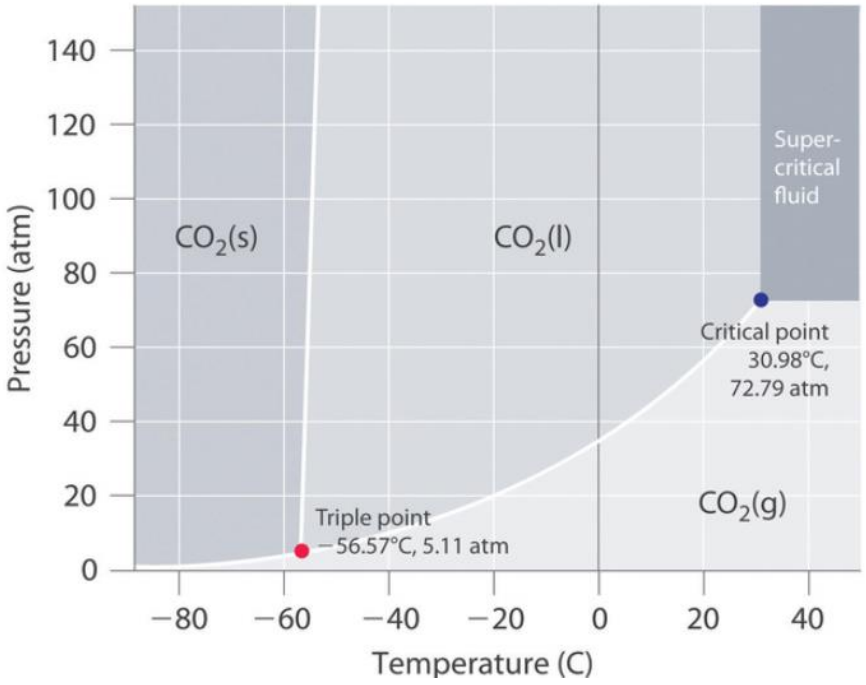

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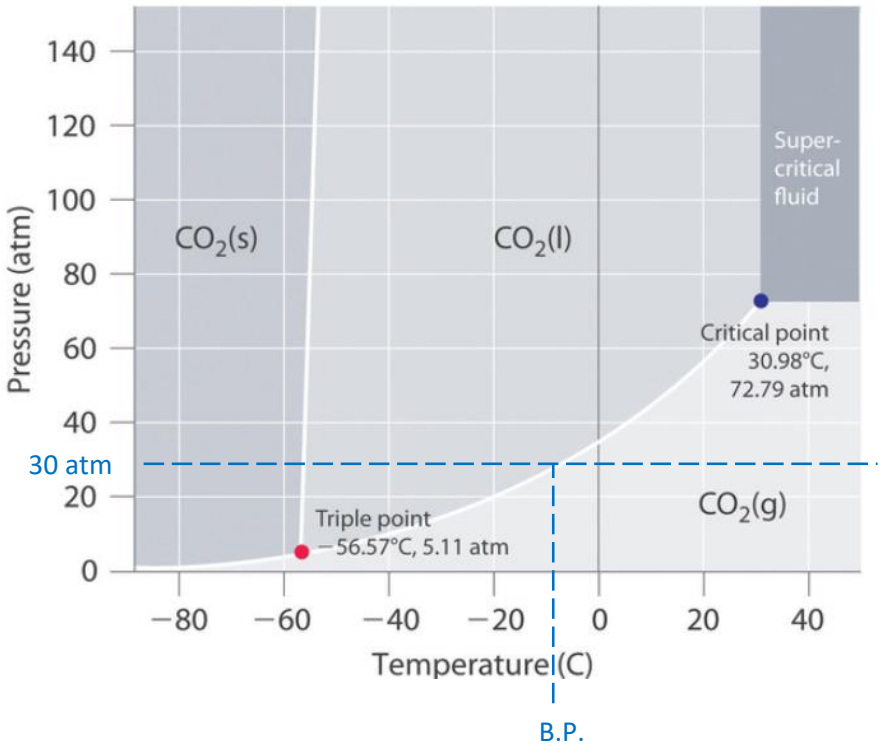
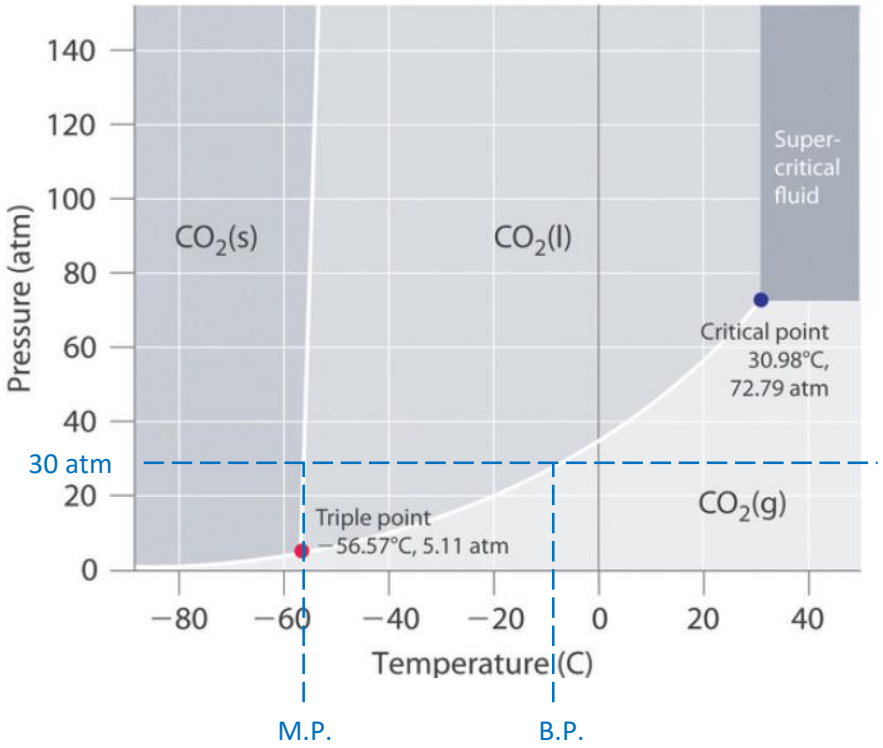
- Phase boundaries (lines) are determined by the condition that the chemical potentials of the two phases are equal.
- Three phase boundaries meet at the triple point – three different phases of the substance are in equilibrium.
- The critical point marks the highest T and P at which the liquid and gas phases coexist.
- CO_2's triple point marks the lowest P (and T) at which a liquid phase can exist. Below 5.11 atm, dry ice sublimates.

Phase diagram – CO_2



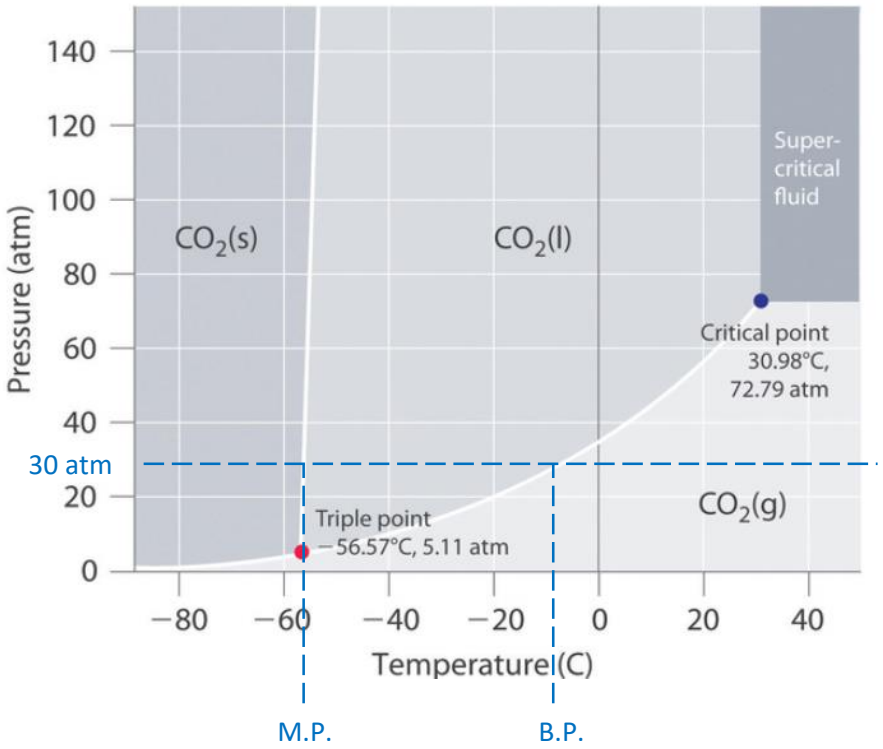
- The point where your horizontal line intersects the L-V boundary represents the boiling point at that P

Phase diagram – CO_2



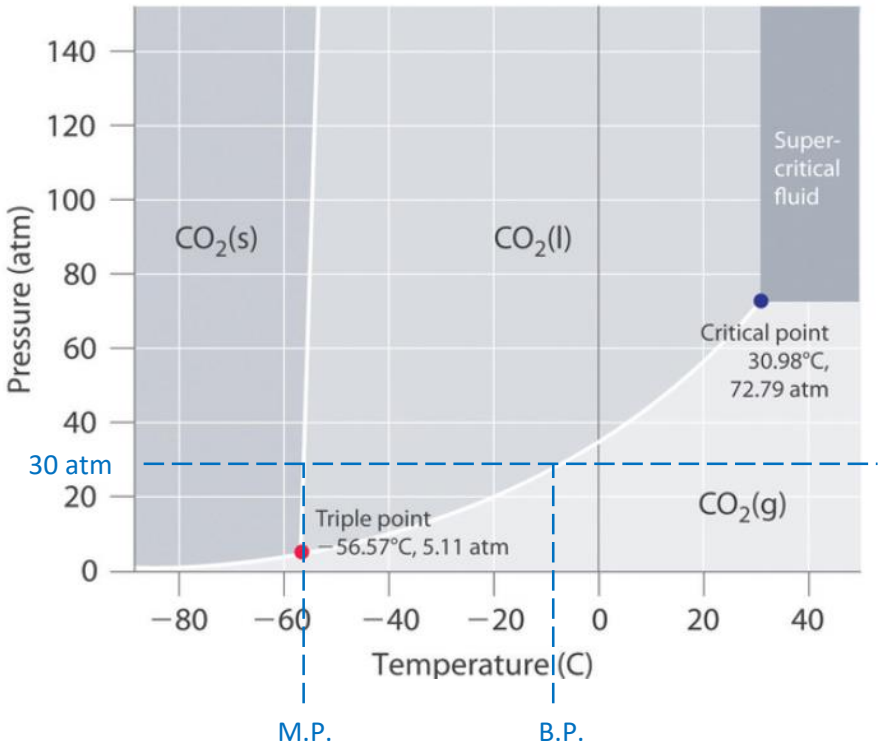
- The point where your horizontal line intersects the L-V boundary represents the boiling point at that P
- The point where your horizontal line intersects the S-L boundary represents the melting (freezing) point at that P

Phase diagram – CO_2



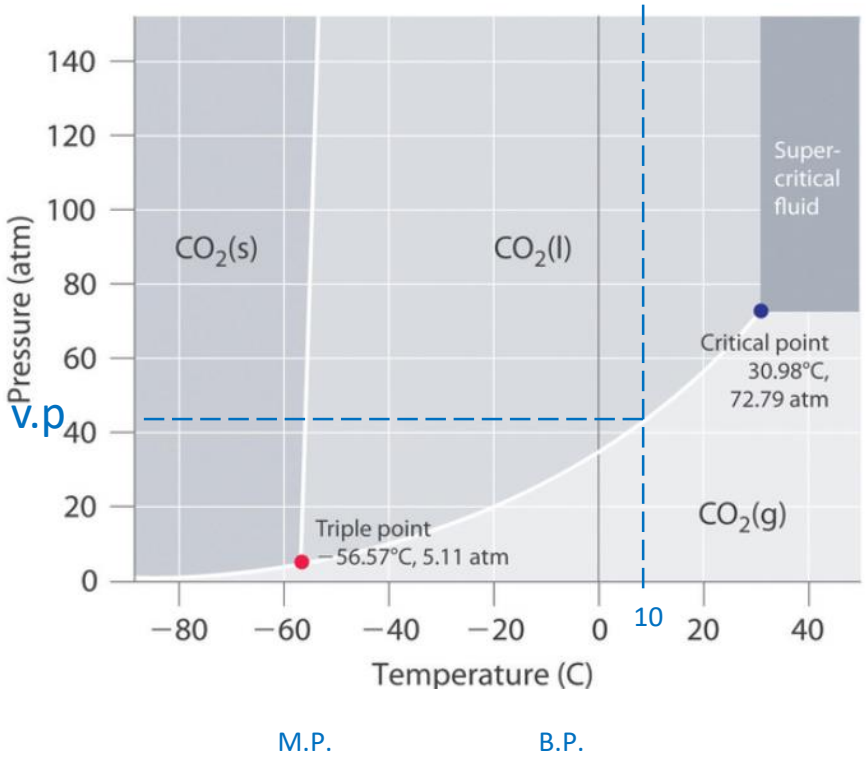
- The point where your horizontal line intersects the L-V boundary represents the boiling point at that P
- The point where your horizontal line intersects the S-L boundary represents the melting (freezing) point at that P
- The point where your horizontal line intersects the S-V boundary represents the sublimation point at that P

Phase diagram – CO_2



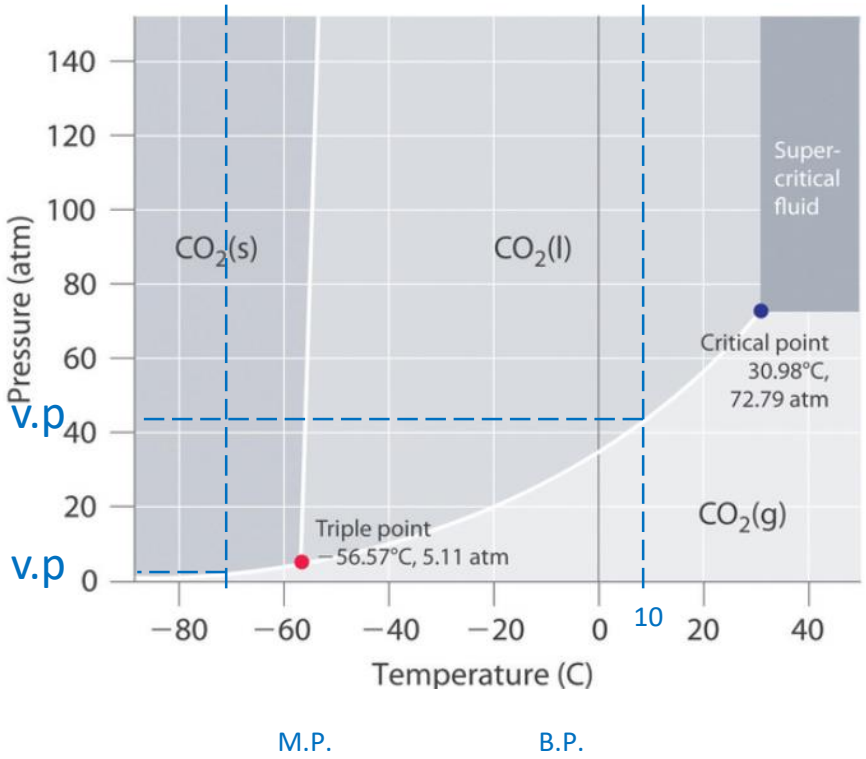
- The point where your horizontal line intersects the L-V boundary represents the boiling point at that P
- The point where your horizontal line intersects the S-L boundary represents the melting (freezing) point at that P
- The point where your horizontal line intersects the S-V boundary represents the sublimation point at that P
- The melting point of CO_2 increases more significantly with pressure compared to the boiling point or sublimation point.

Phase diagram – CO_2



- The liquid-vapor (L-V) boundary represents the pressure of the vapor that is in equilibrium with the liquid at different temperatures.

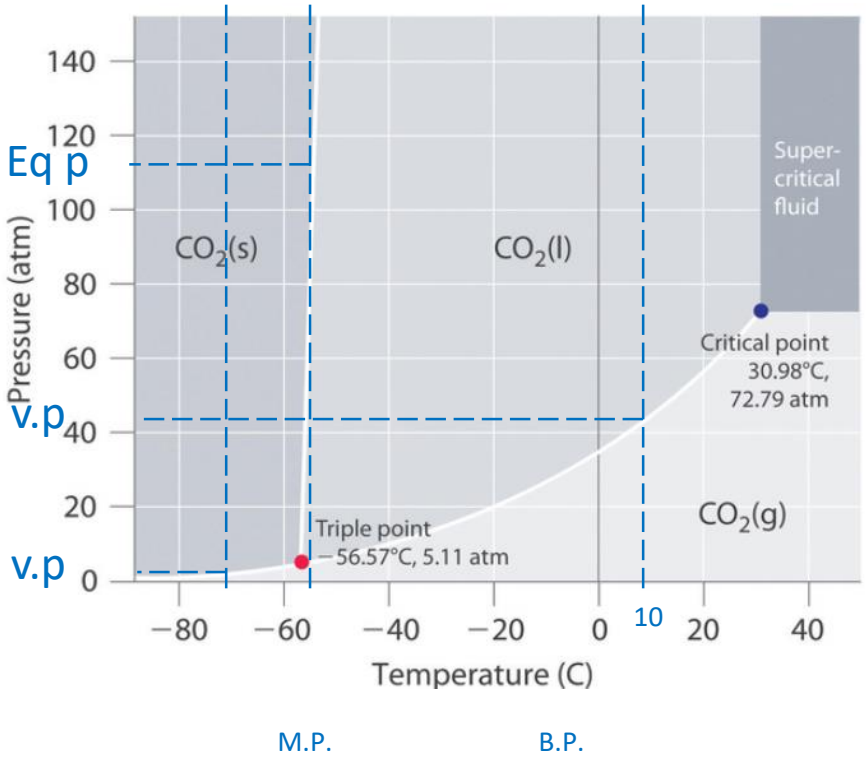
Phase diagram – CO_2



- The liquid-vapor (L-V) boundary represents the pressure of the vapor that is in equilibrium with the liquid at different temperatures.

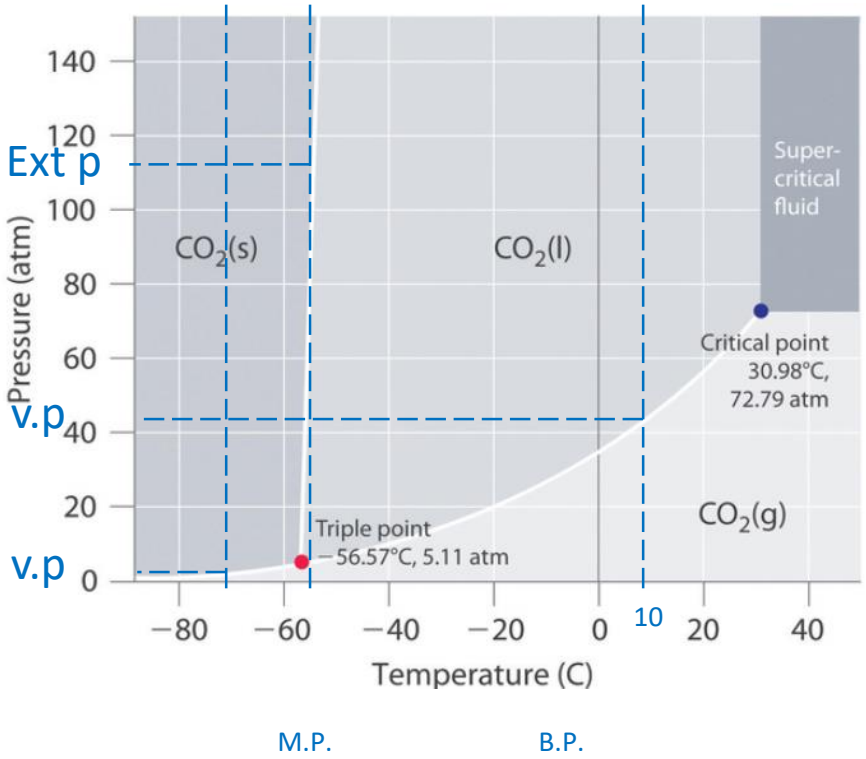
- The solid-vapor (S-V) boundary represents the pressure of the vapor that is in equilibrium with the solid at different temperatures.

Phase diagram – CO_2



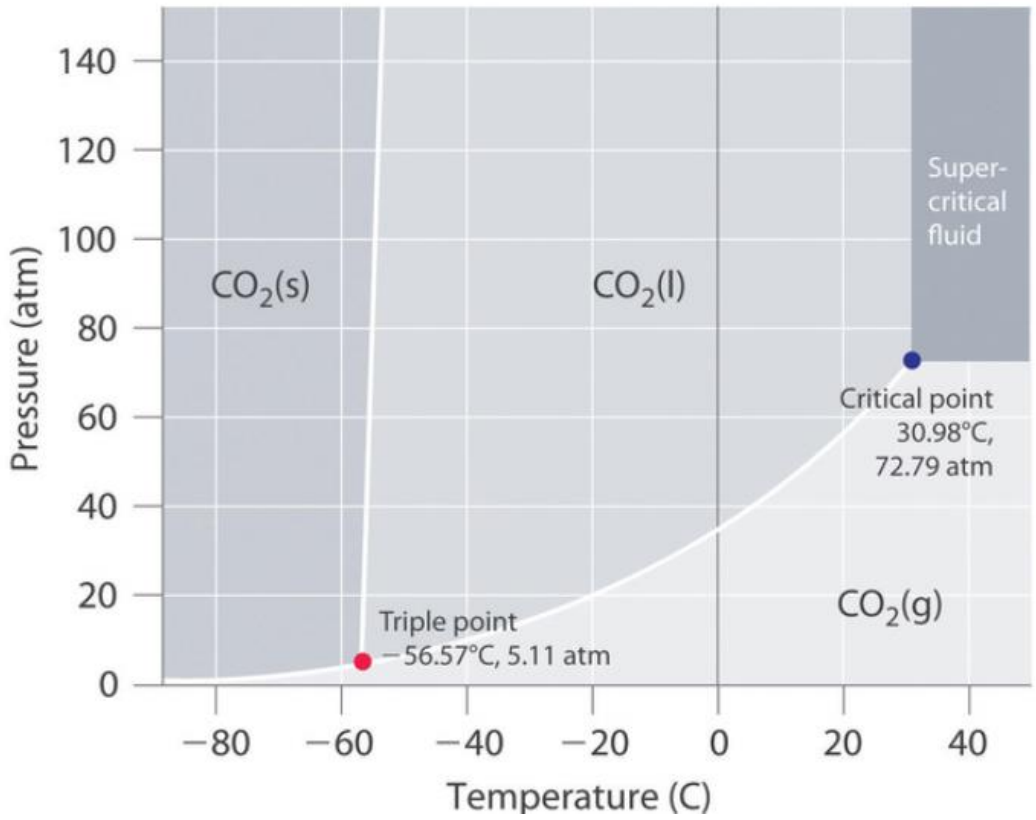
- The liquid-vapor (L-V) boundary represents the pressure of the vapor that is in equilibrium with the liquid at different temperatures.
- The solid-vapor (S-V) boundary represents the pressure of the vapor that is in equilibrium with the solid at different temperatures.
- The solid-liquid (S-L) boundary represents the equilibrium pressure at which a substance transitions between the solid and liquid phases at different temperatures

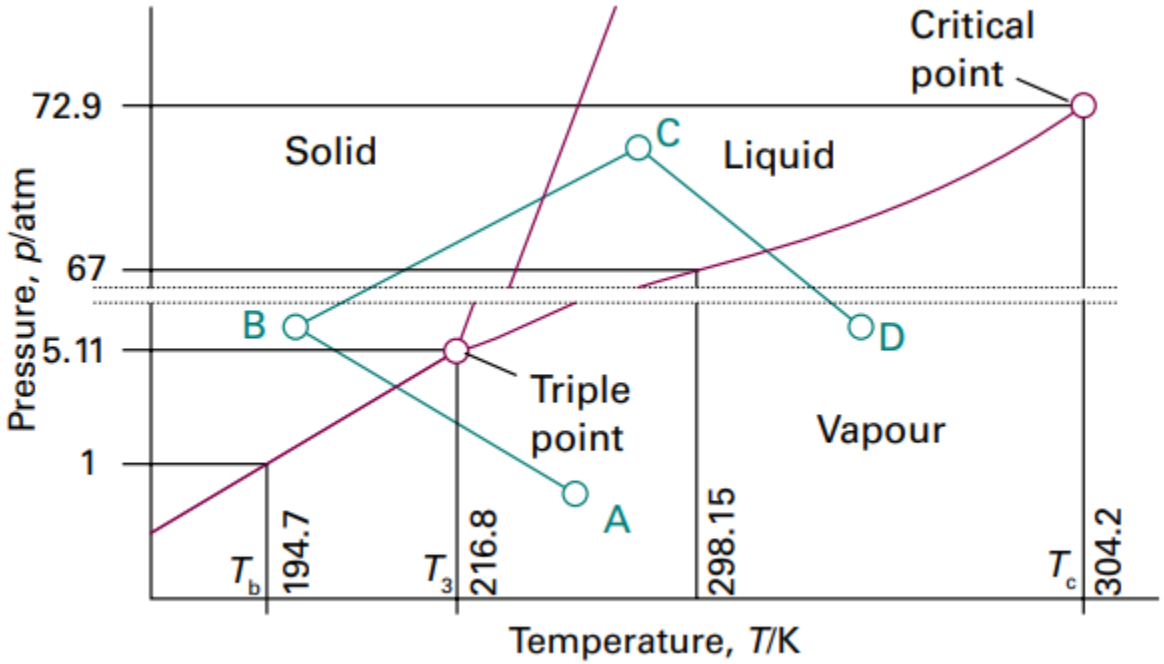
Phase diagram – CO_2



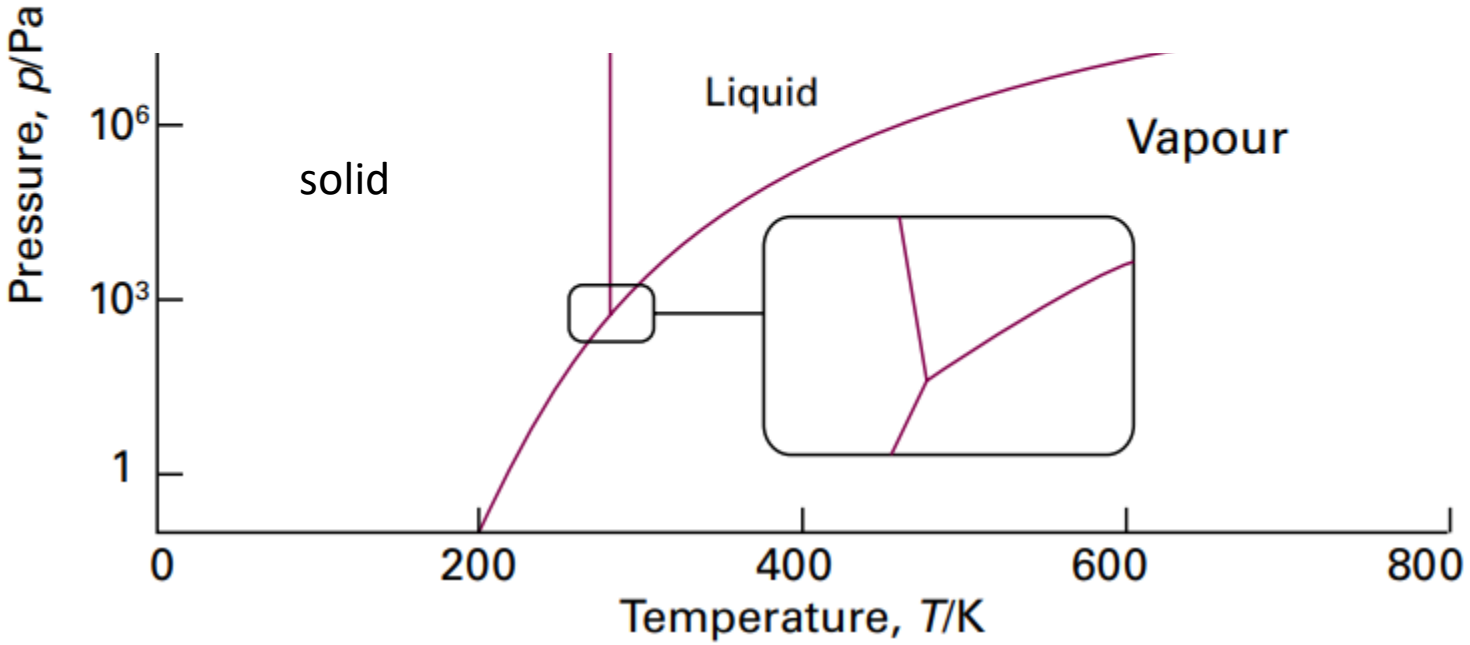
- The liquid-vapor (L-V) boundary represents the pressure of the vapor that is in equilibrium with the liquid at different temperatures.
- The solid-vapor (S-V) boundary represents the pressure of the vapor that is in equilibrium with the solid at different temperatures.
- The solid-liquid (S-L) boundary represents the equilibrium pressure at which a substance transitions between the solid and liquid phases at different temperatures
- Pressure represented along the solid-liquid (S-L) boundary is the external pressure applied to the system. Unlike the L-V or S-V boundaries, where vapor pressure plays a role, the S-L boundary does not involve a gas phase, so there's no vapor pressure.

Phase diagram – CO_2



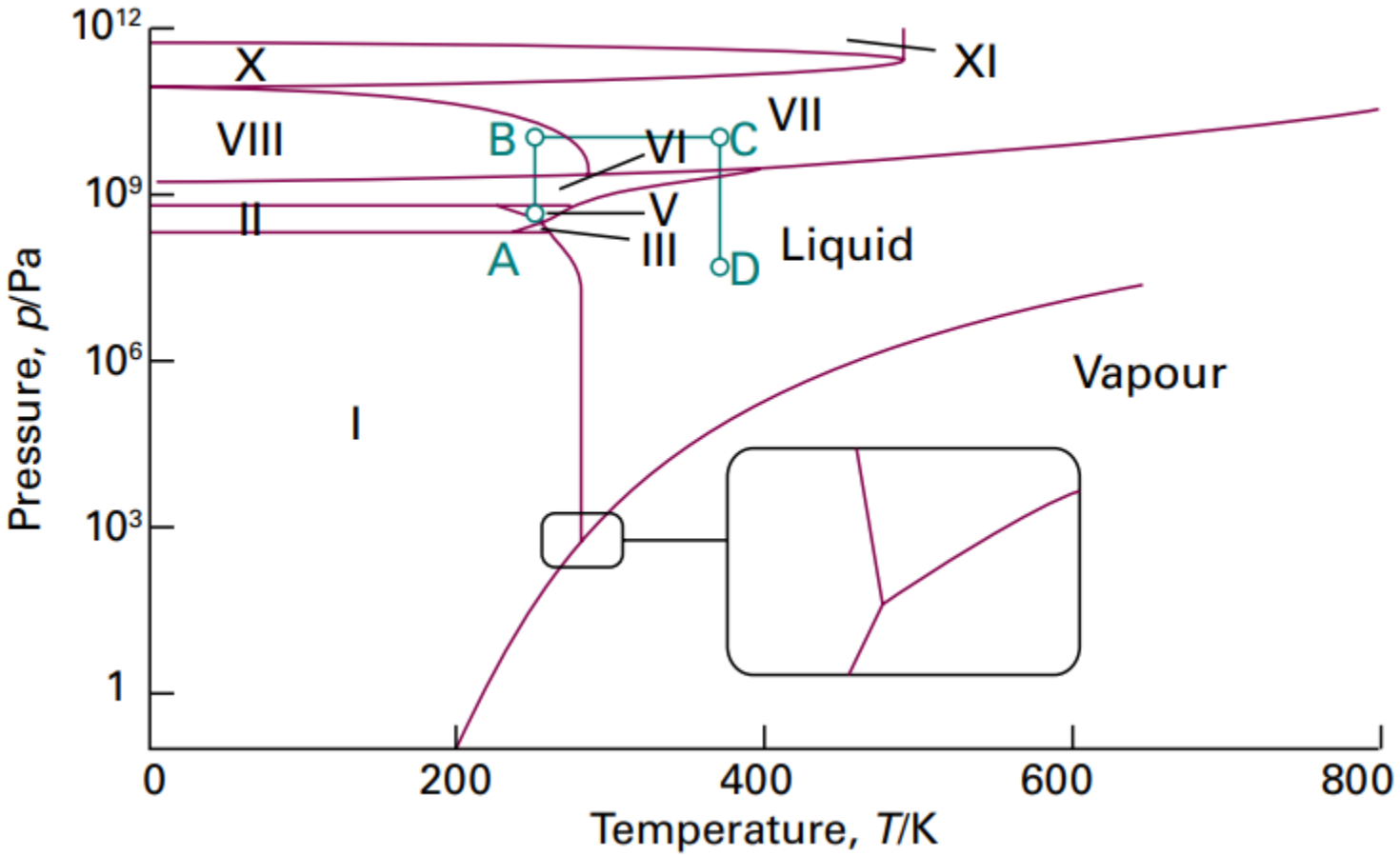


Phase diagram – H_2O



$1\ \text{atm} = 101,325\ \text{Pa}$

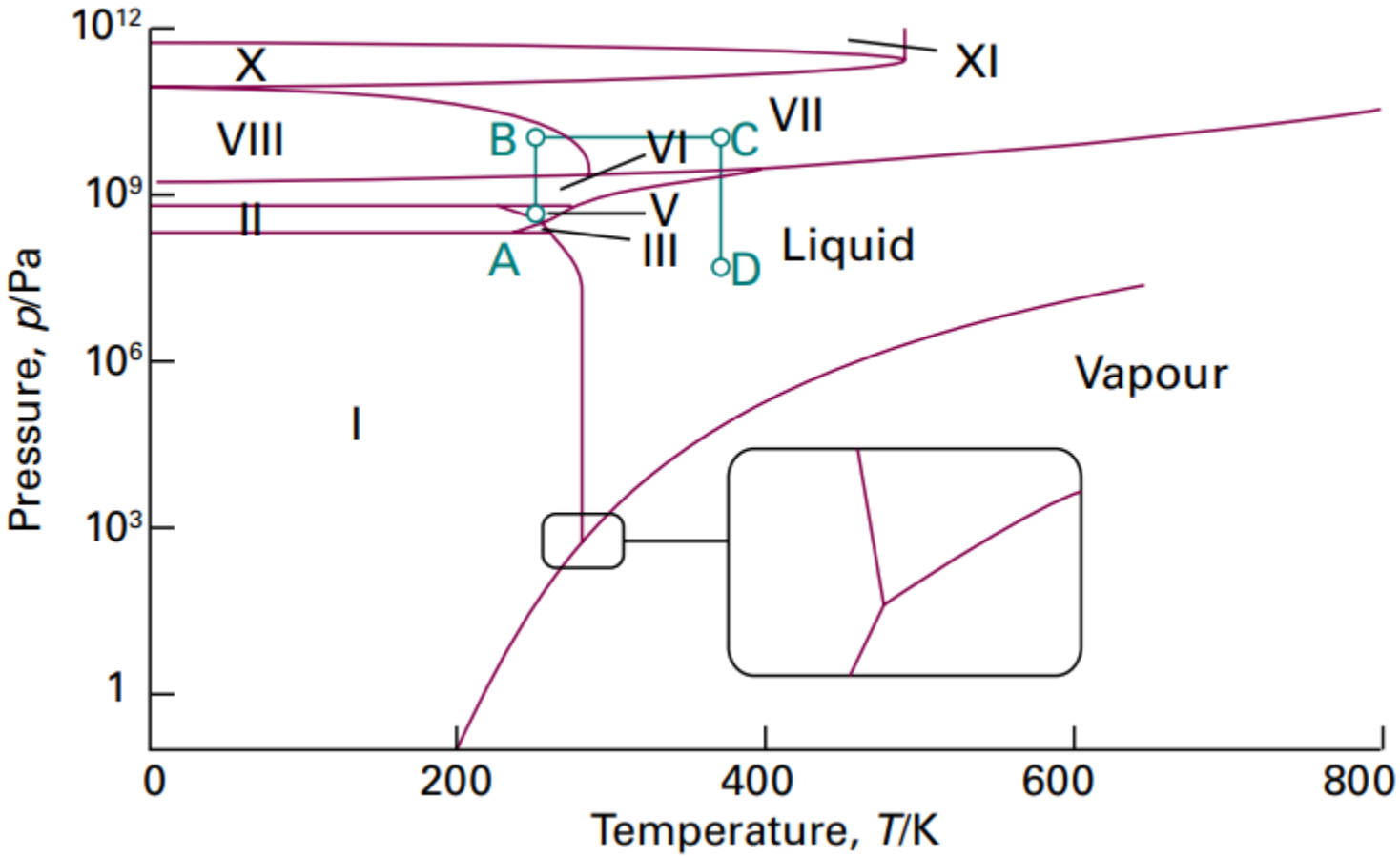
Phase diagram – H_2O



Different solid phases are indicated with Roman numerals I, II,…

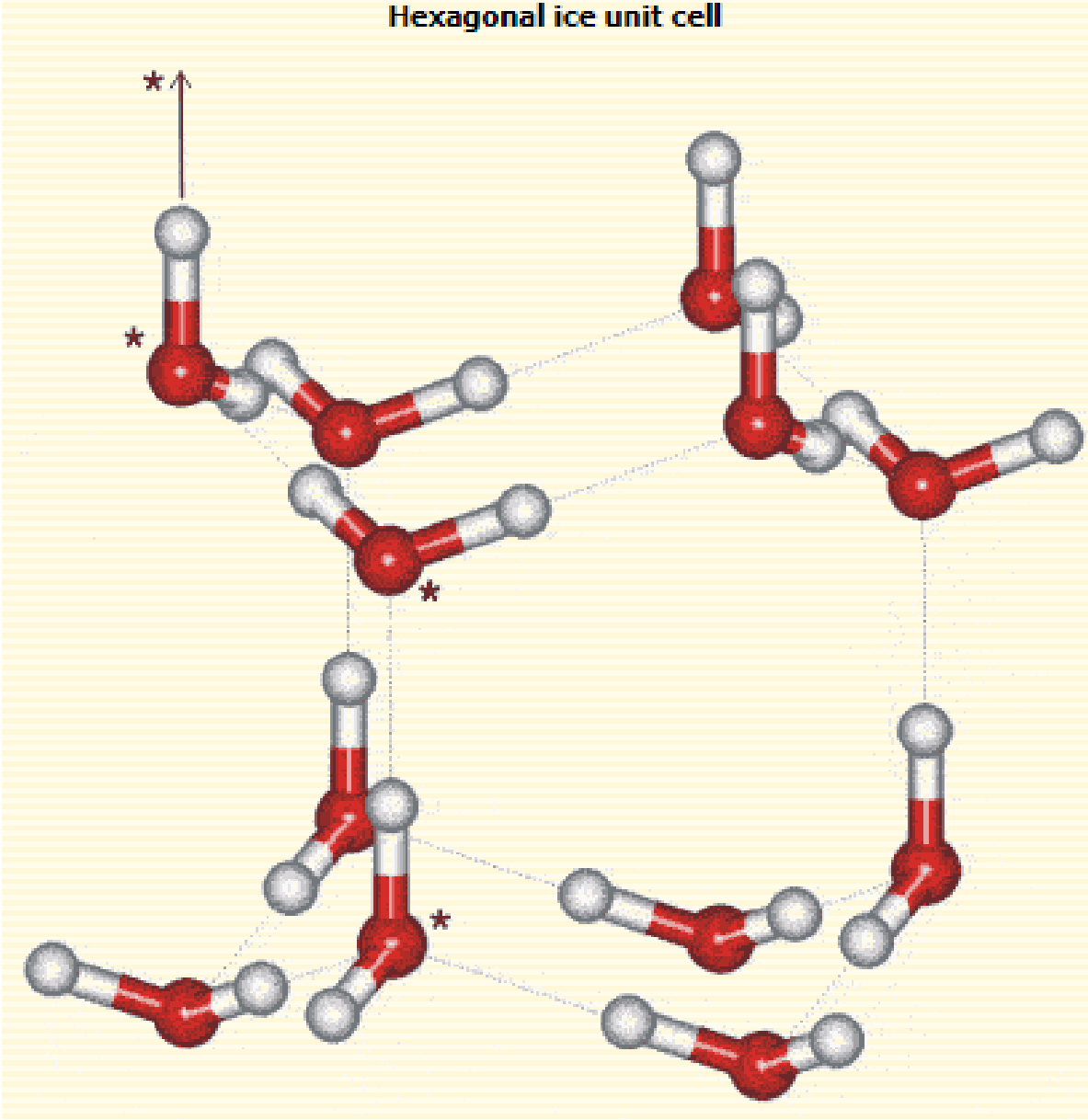
$1\ \text{atm} = 101,325\ \text{Pa}$

Phase diagram – H_2O



Different solid phases are indicated with Roman numerals I, II,…

ice I_h



Hexagonal ice, denoted as Ice Ih, is the most common form of ice found on Earth.

It has a hexagonal closed packed (hcp) crystalline structure and is the stable phase of ice at atmospheric pressure and temperatures below 0°C (273 K).

Ice phases

nature COMMUNICATIONS

COMMENT

https://doi.org/10.1038/s41467-021-23403-6 OPEN

The everlasting hunt for new ice phases

Thomas C. Hansen [1]✉

Water ice exists in hugely different environments, artificially or naturally occurring ones across the universe. The phase diagram of crystalline phases of ice is still under construction: a high-pressure phase, ice XIX, has just been reported but its structure remains ambiguous.

Ice phases

Polymorphs - Different crystalline forms of the same compound

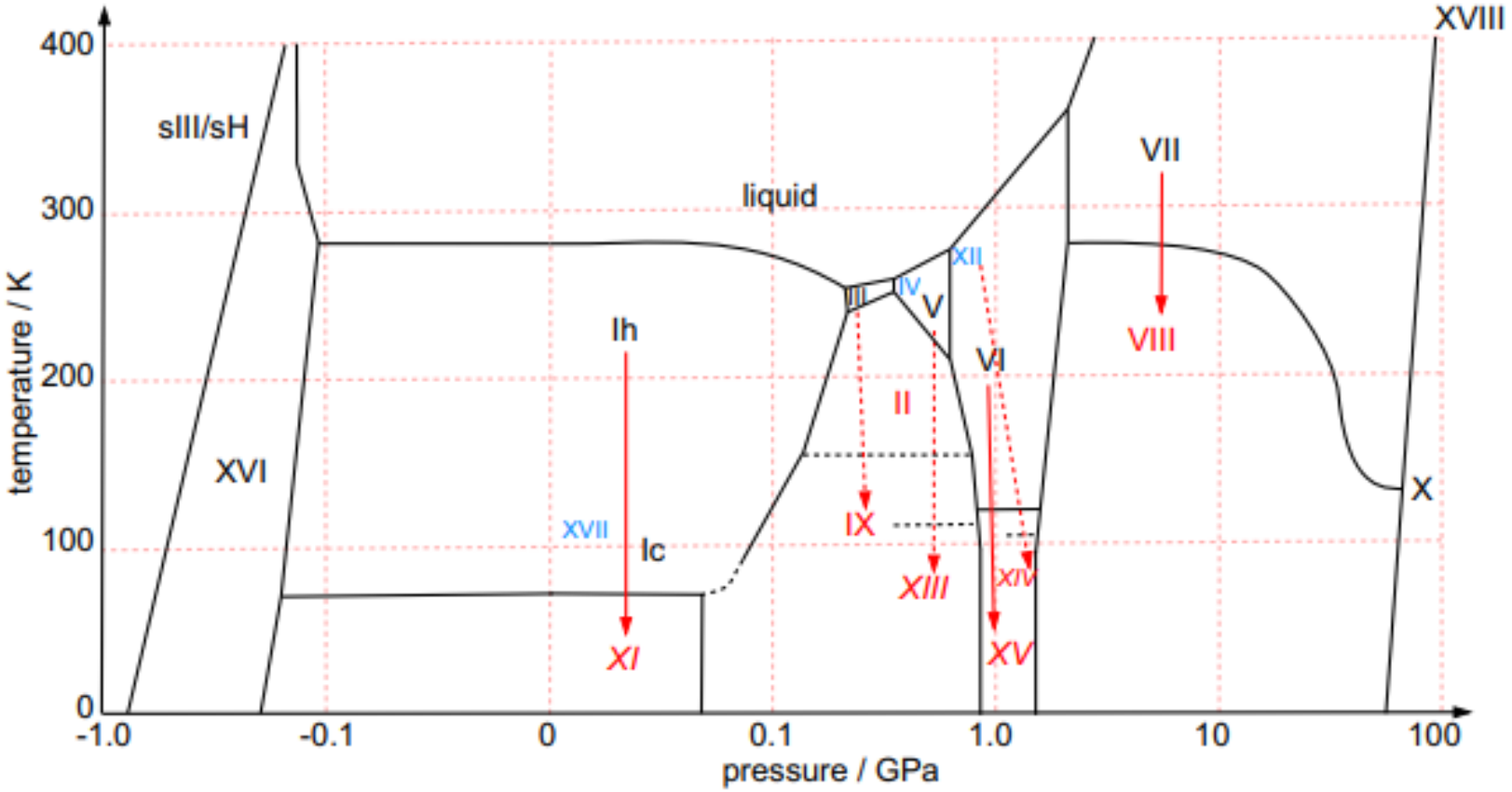
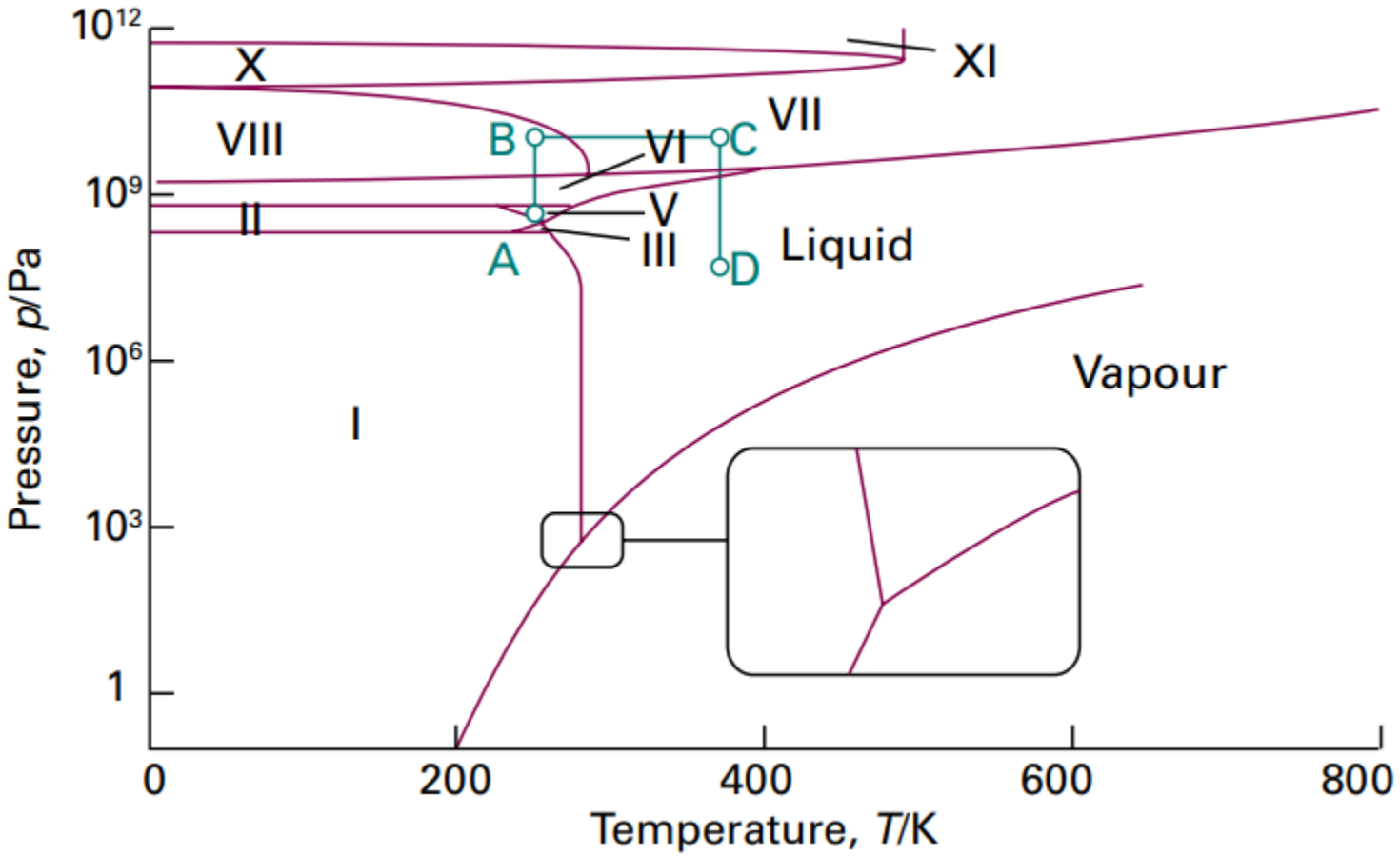


Fig. 1 Schematic phase diagram of crystalline ice phases inspired by Bartels-Rausch et al.[1], Salzmann et al.[18] and Huang et al.[21]. Phases

Ice polymorph
Hexagonal ice, Ih
Cubic ice, Ic
LDA, Ia [b]
HDA [c]
VHDA [d]
II, Ice-two
III, Ice-three
IV, Ice-four
V, Ice-five
VI, Ice-six
VII, Ice-seven
VIII, Ice-eight
IX, Ice-nine
X, Ice-ten
XI, Ice-eleven
XI, Ice-eleven[k]
Metallic [1818] [k]
XII, Ice-twelve
XIII, Ice-thirteen
XIV, Ice-fourteen
XV, Ice-fifteen

Phase diagram – H_2O



Different solid phases are indicated with Roman numerals I, II,…

H_2O vs D_2O

H_2O vs D_2O

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Phase Diagrams of H_2O and D_2O at High Pressures

CARL W. F. T. PISTORIUS, ELIEZER RAPOPORT, AND J. B. CLARK

Chemical Physics Group of the National Physical and National Chemical Research Laboratories, South African Council for Scientific and Industrial Research, P.O. Box 395, Pretoria, South Africa

(Received 26 December 1967)

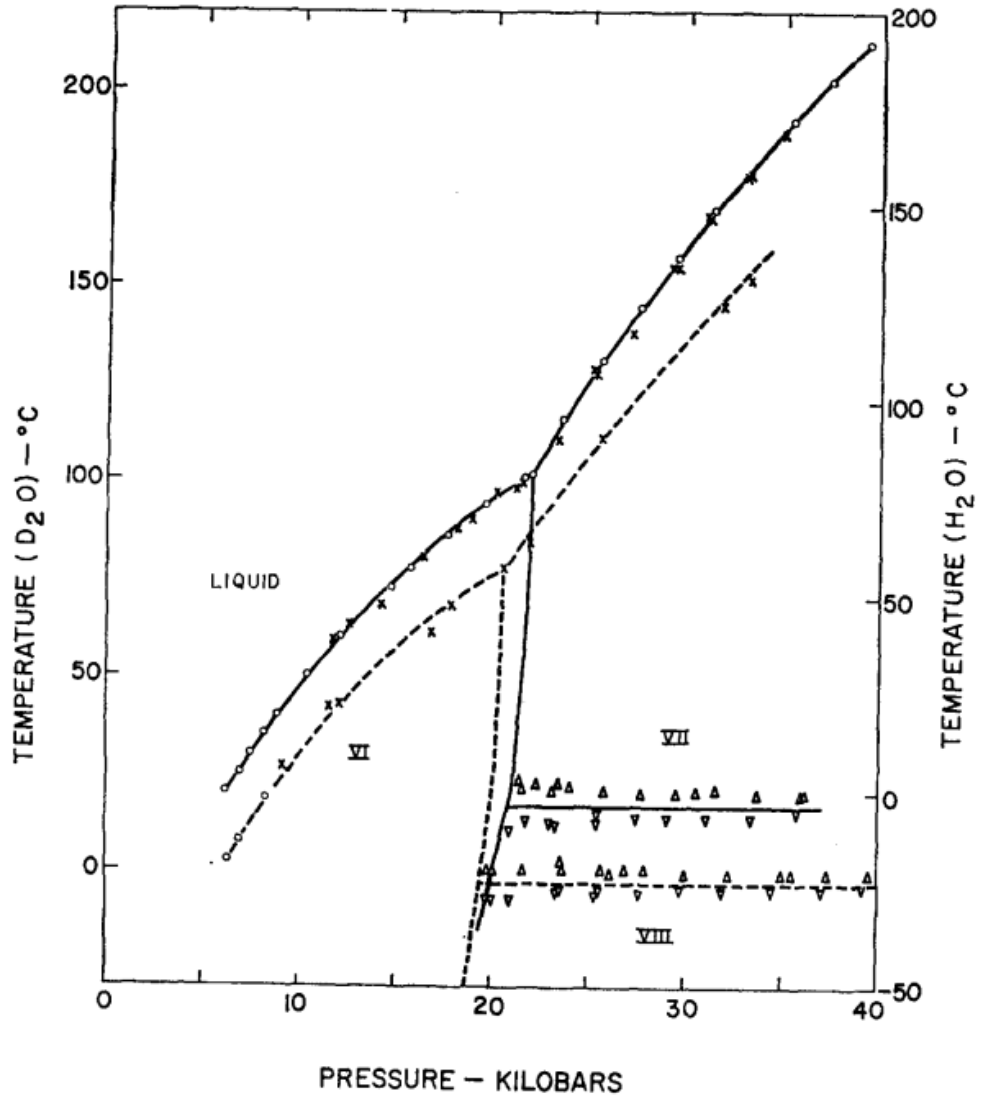
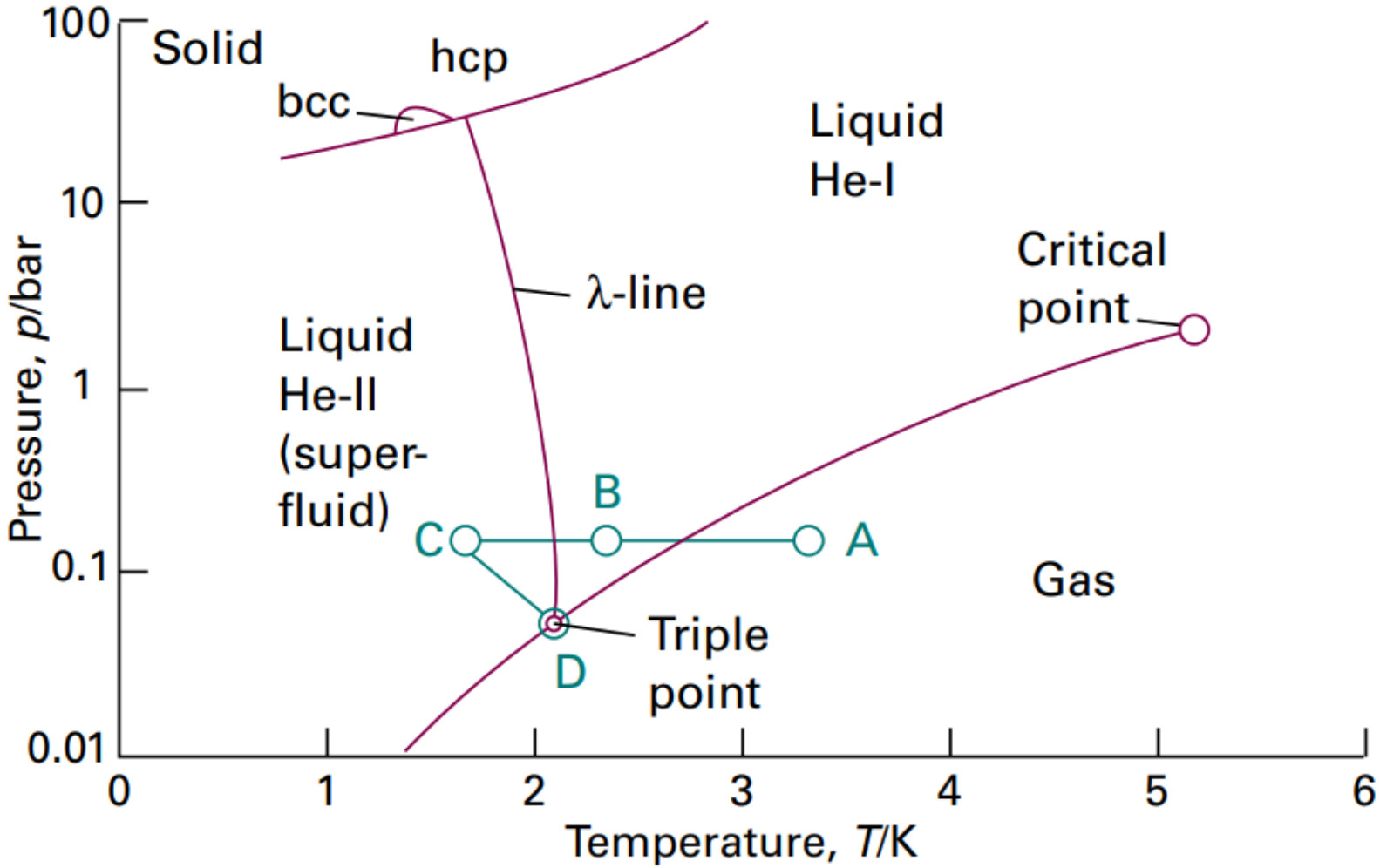


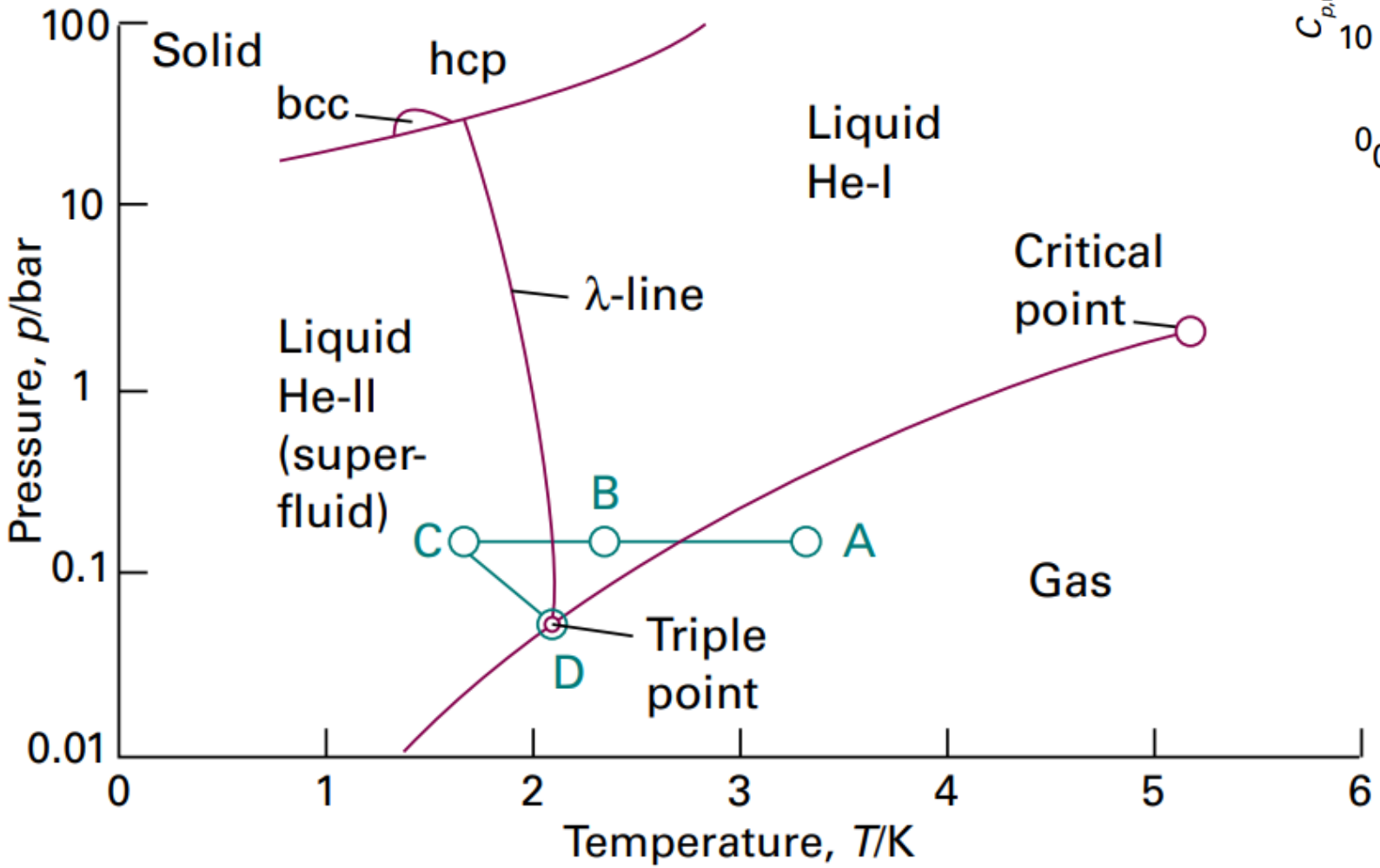
FIG. 3. The phase diagrams of H_2O and D_2O to 40 kbar. The points for H_2O are raised 20°C above those for D_2O for the sake of clarity. D_2O— broken line; H_2O— solid line. ○—Bridgman (1935, 1937); ×—present work melting; △—present work heating; ▽—present work cooling.

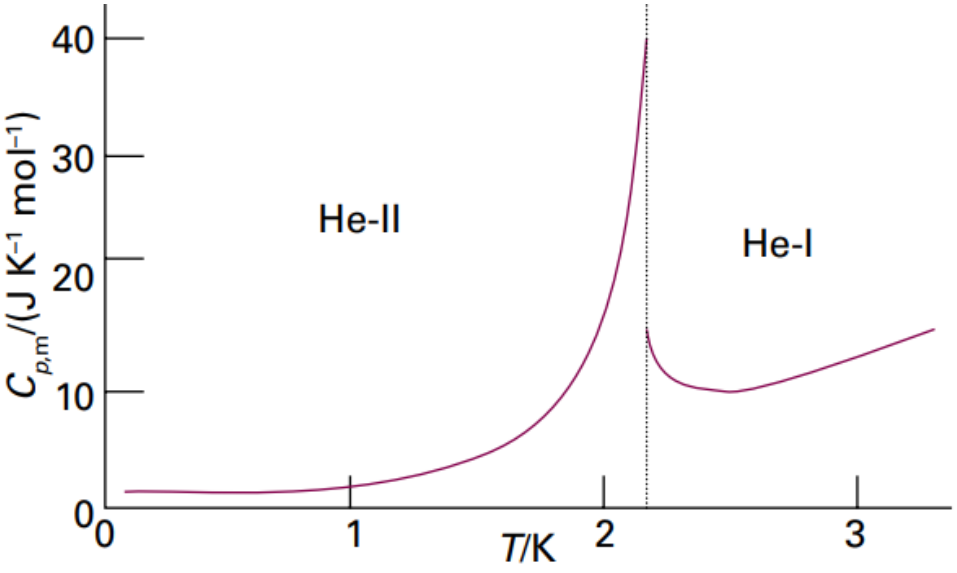
Lower ZPE in D_2O means hydrogen bonds are shorter and stronger, requiring more energy to break.

Helium


100
10
1
0.1
0.01
Pressure, p/bar
0
1
2
3
4
5
6
Temperature, T/K
Solid
hcp
bcc
Liquid
He-I
λ-line
Critical
point
Liquid
He-II
(super-
fluid)
B
C
A
Gas
Triple
point
D

Helium


Solid
hcp
bcc
Liquid
He-I
λ-line
Critical
point
Liquid
He-II
(super-
fluid)
B
C
A
Gas
Triple
point
D
100
10
1
0.1
0.01
Pressure, p/bar
0
1
2
3
4
5
6
Temperature, T/K


40
30
20
10
0
$C_{p,m}$/(J K^{-1} mol^{-1})
He-II
He-I
0
1
T/K
2
3

Letters to the Editor

The Editor does not hold himself responsible for opinions expressed by his correspondents. He cannot undertake to return, or to correspond with the writers of, rejected manuscripts intended for this or any other part of NATURE. *No notice is taken of anonymous communications.*

NOTES ON POINTS IN SOME OF THIS WEEK'S LETTERS APPEAR ON P. 83.

CORRESPONDENTS ARE INVITED TO ATTACH SIMILAR SUMMARIES TO THEIR COMMUNICATIONS.

Viscosity of Liquid Helium below the λ-Point

THE abnormally high heat conductivity of helium II below the λ-point, as first observed by Keesom, suggested to me the possibility of an explanation in terms of convection currents. This explanation would require helium II to have an abnormally low viscosity; at present, the only viscosity measurements on liquid helium have been made in Toronto[1], and showed that there is a drop in viscosity below the λ-point by a factor of 3 compared with liquid helium at normal pressure, and by a factor of 8 compared with the value just above the λ-point. In these experiments, however, no check was made to ensure that the motion was laminar, and not turbulent.

The important fact that liquid helium has a specific density ρ of about 0·15, not very different from that of an ordinary fluid, while its viscosity μ is very small comparable to that of a gas, makes its

tube 3 could be set above or below the level (5) of the liquid in the surrounding Dewar flask. The amount of flow and the pressure were deduced from the difference of the two levels, which was measured by cathetometer.

The results of the measurements were rather striking. When there were no distance pieces between the disks, and the plates 1 and 2 were brought into contact (by observation of optical fringes, their separation was estimated to be about half a micron), the flow of liquid above the λ-point could be only just detected over several minutes, while below the λ-point the liquid helium flowed quite easily, and the level in the tube 3 settled down in a few seconds. From the measurements we can conclude that the viscosity of helium II is at least 1,500 times smaller than that of helium I at normal pressure.

The experiments also showed that in the case of helium II, the pressure drop across the gap was

Nobel Prize in Physics 1996

Photo from the Nobel Foundation archive.

David M. Lee

Prize share: 1/3

Photo from the Nobel Foundation archive.

Douglas D. Osheroff

Prize share: 1/3

Photo from the Nobel Foundation archive.

Robert C. Richardson

Prize share: 1/3

The Nobel Prize in Physics 1996 was awarded jointly to David M. Lee, Douglas D. Osheroff and Robert C. Richardson "for their discovery of superfluidity in helium-3"

LAW - Superfluids climb up the walls of their container due to a phenomenon called the Rollin film effect.

Explain that briefly.

Focus 4: Physical transformation of pure substances

Phase diagrams of pure substances

Thermodynamic aspects of phase transitions

Variation of chemical potential with T and P

Variation of chemical potential with T and P

$$\mu = G_m$$

Variation of chemical potential with T and P

$$\mu = G_m$$

$$dG = -S dT \text{ at constant pressure;}$$
$$dG = V dp \text{ at constant temperature}$$

Variation of chemical potential with T and P

$$\mu = G_m$$

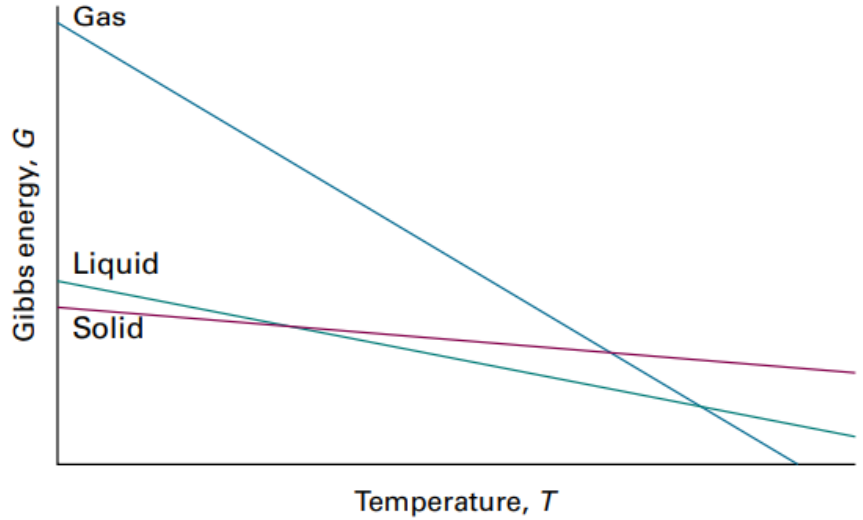
$dG = -S dT$ at constant pressure;
$dG = V dp$ at constant temperature

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m \qquad \left(\frac{\partial \mu}{\partial p}\right)_T = V_m$$

Temperature dependence of phase stability

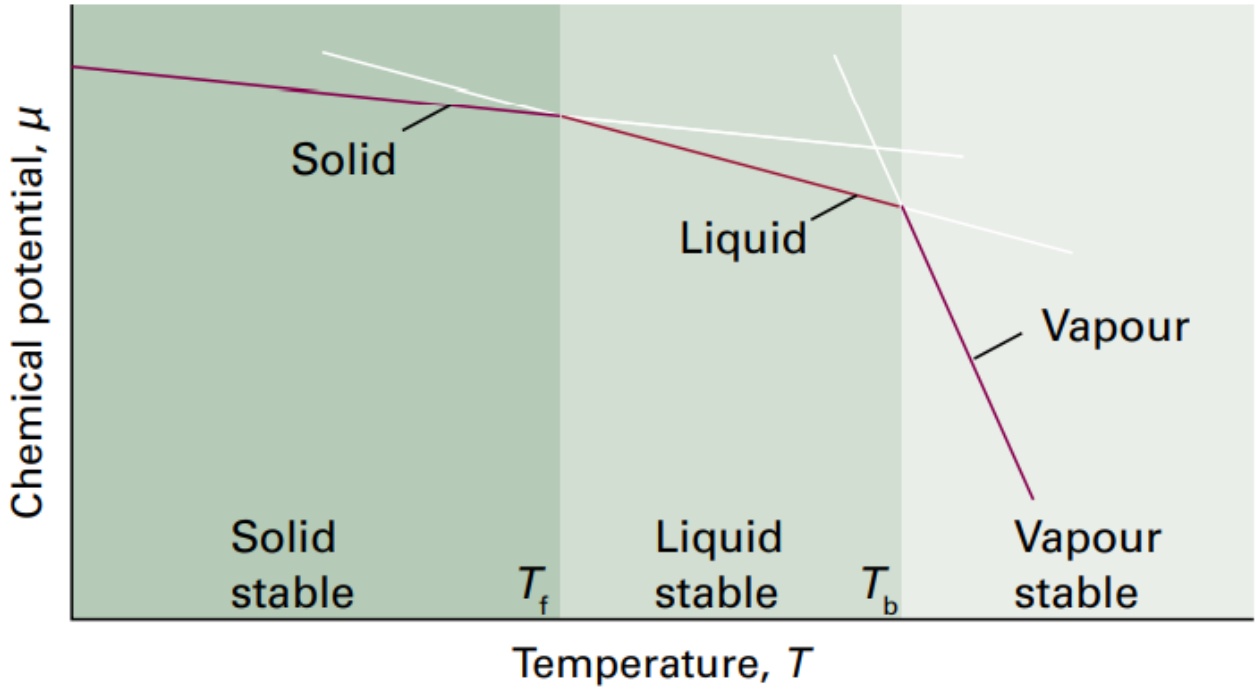
$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$

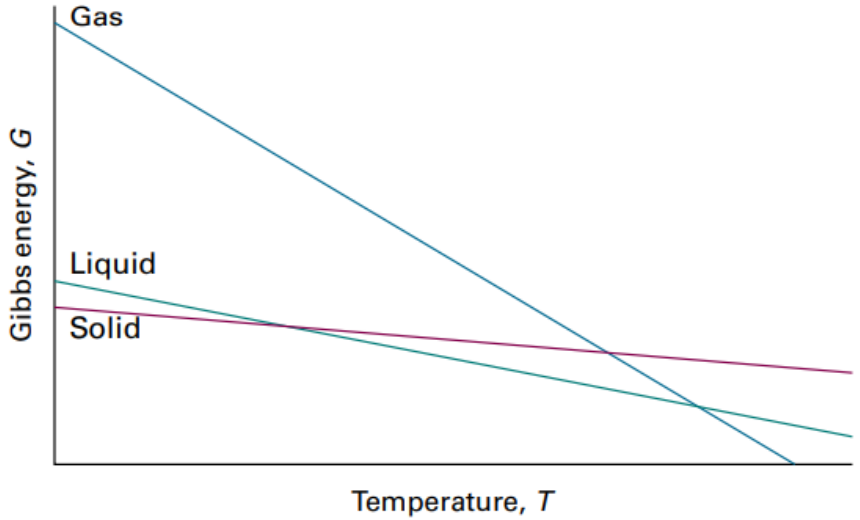
Temperature dependence of phase stability



$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$

Temperature dependence of phase stability





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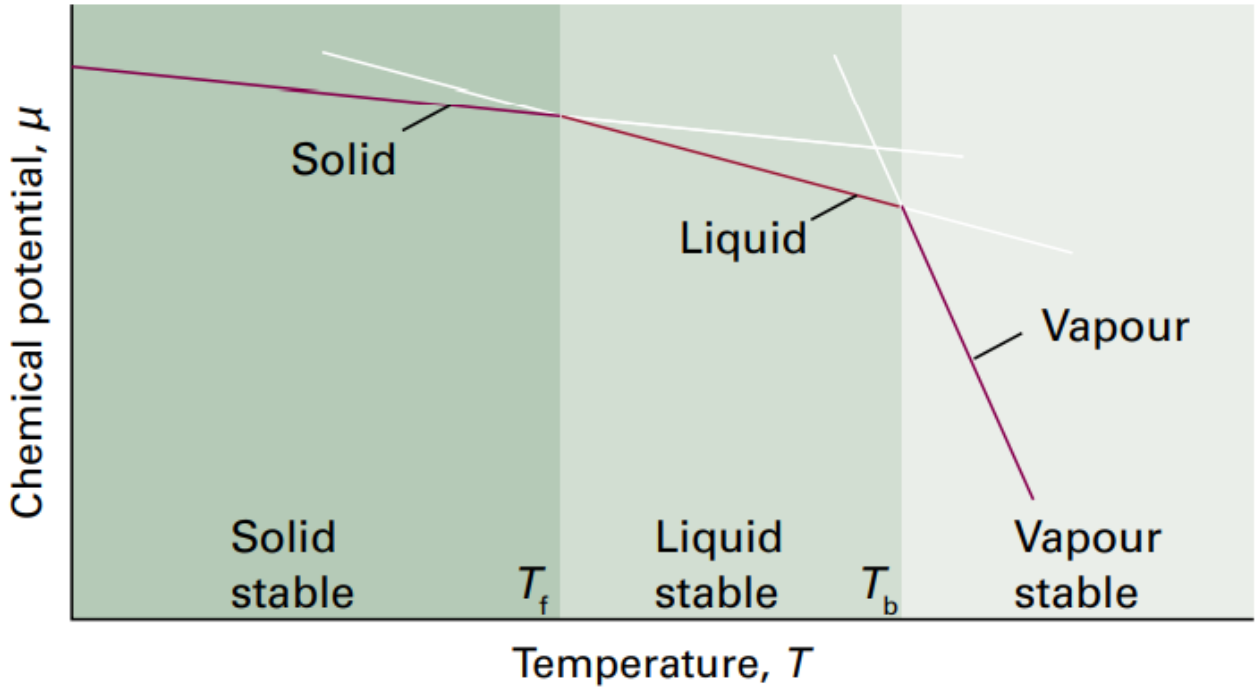
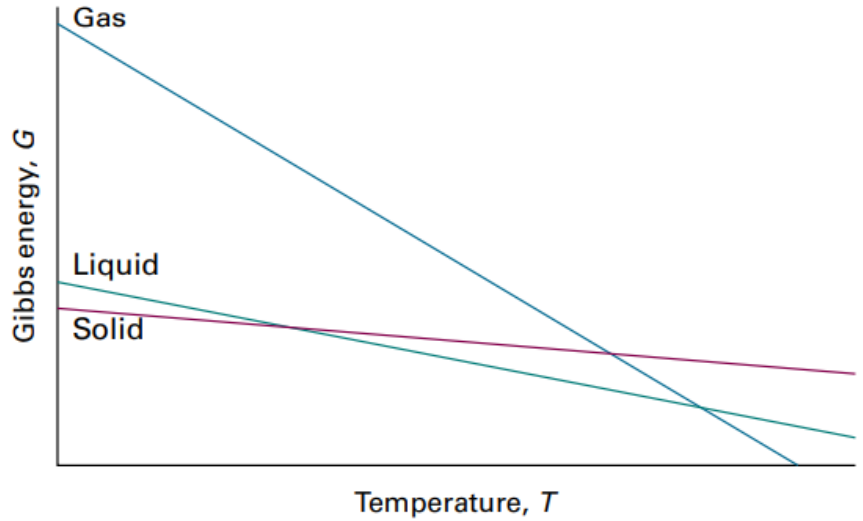
Temperature dependence of phase stability





$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$

The phase with the lowest chemical potential at a specified temperature is the most stable one at that temperature!

Temperature dependence of phase stability

The standard molar entropy of liquid water at 100 °C is $86.8\,J\,K^{-1}\,mol^{-1}$ and that of water vapour at the same temperature is $195.98\,J\,K^{-1}\,mol^{-1}$. It follows that when the temperature is raised by 1.0 K the changes in chemical potential are

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$$\Delta\mu(\mathrm{l}) \approx -S_\mathrm{m}(\mathrm{l})\Delta T$$
$$\Delta\mu(\mathrm{g}) \approx -S_\mathrm{m}(\mathrm{g})\Delta T$$

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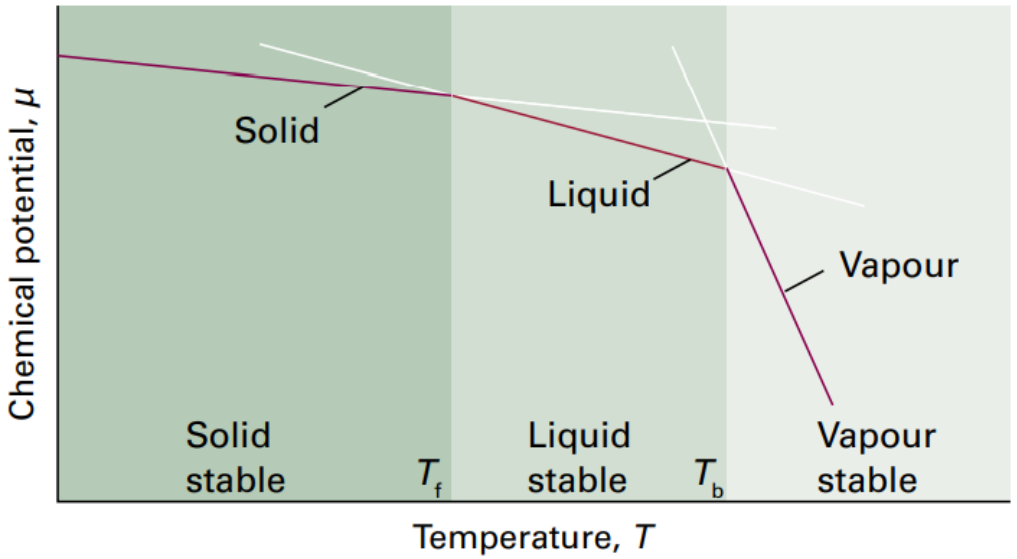
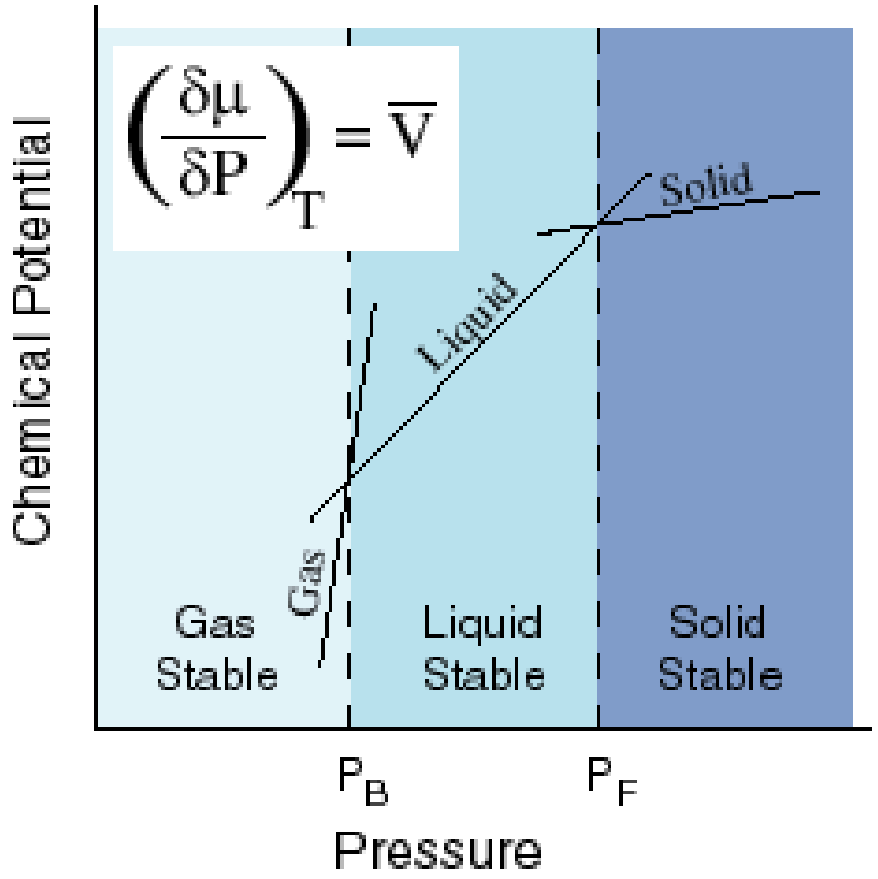


Pressure dependence of phase stability

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_{\mathrm{m}}$$

Pressure dependence of phase stability



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LAW: The response of melting to applied pressure

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Ice melting under pressure

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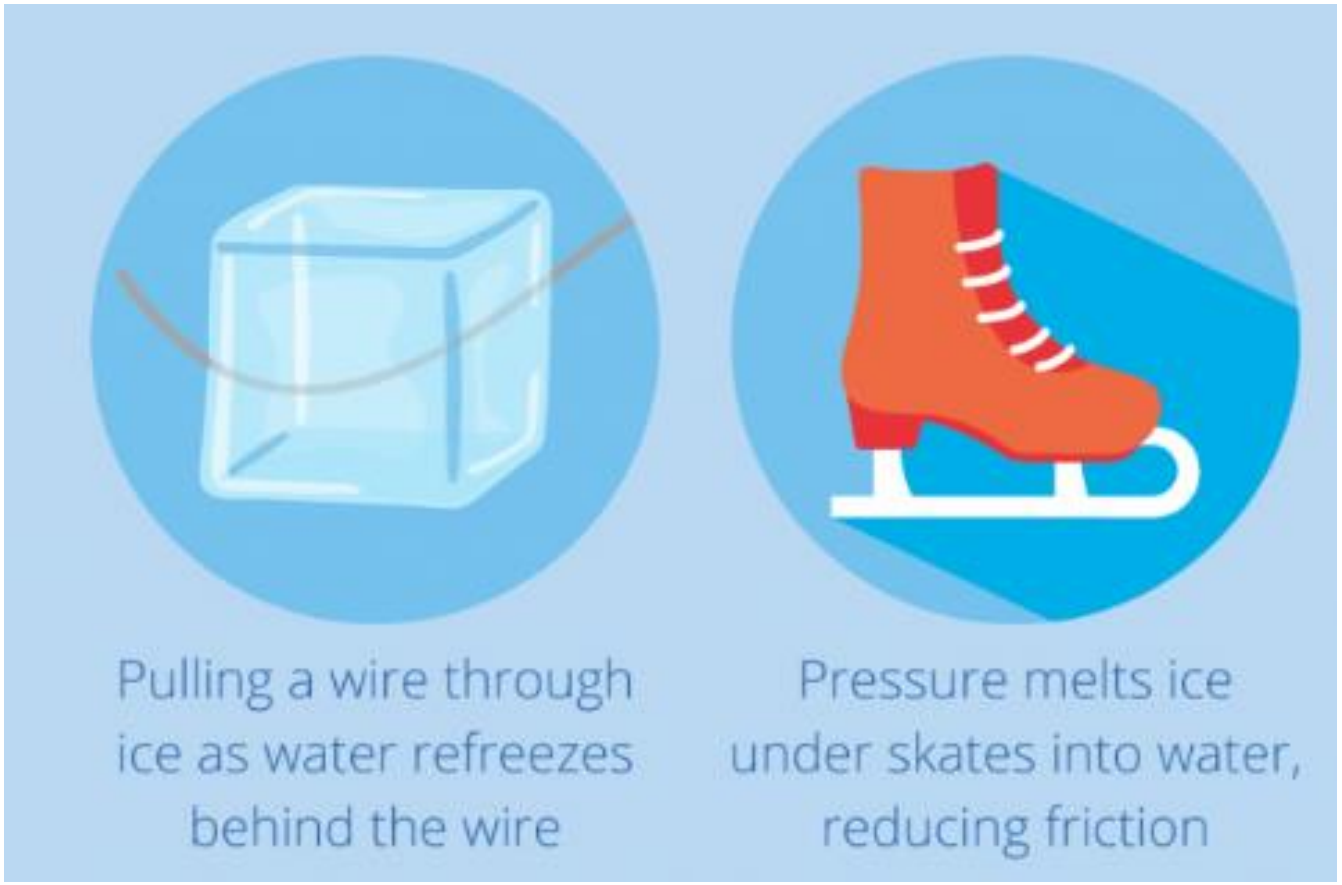

Ice melting under pressure