Statistical Molecular Thermodynamics

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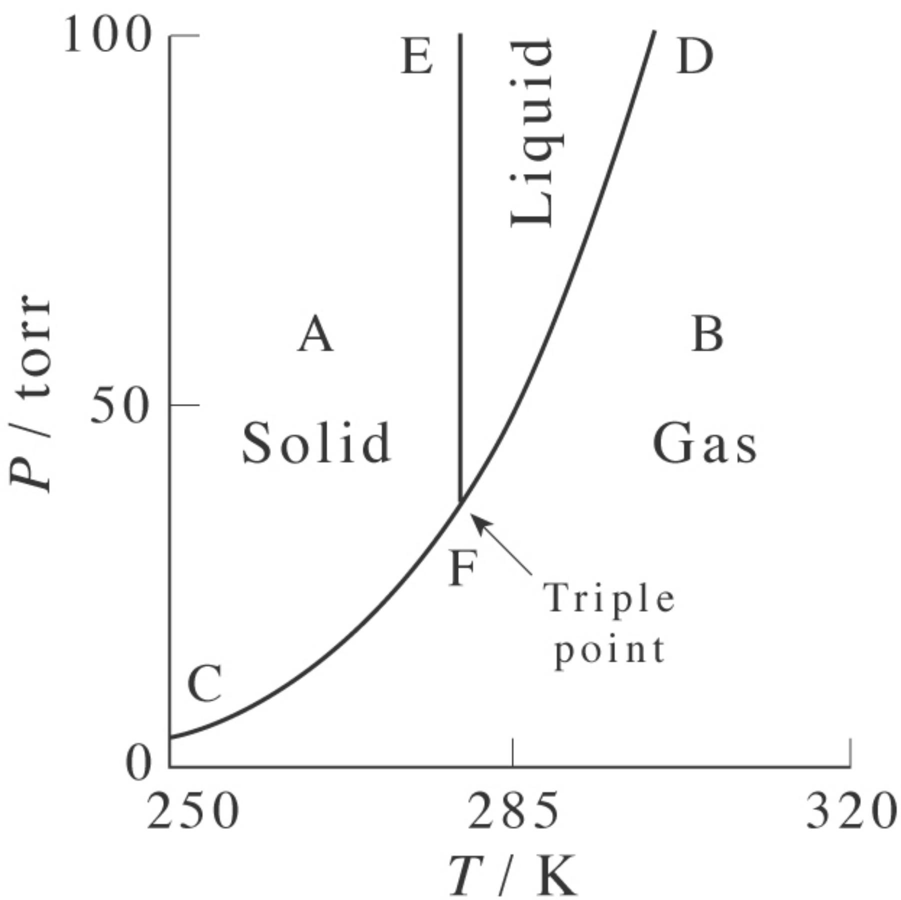
Video 9.1

Phase Equilibria and Phase Diagrams

Phase Diagram

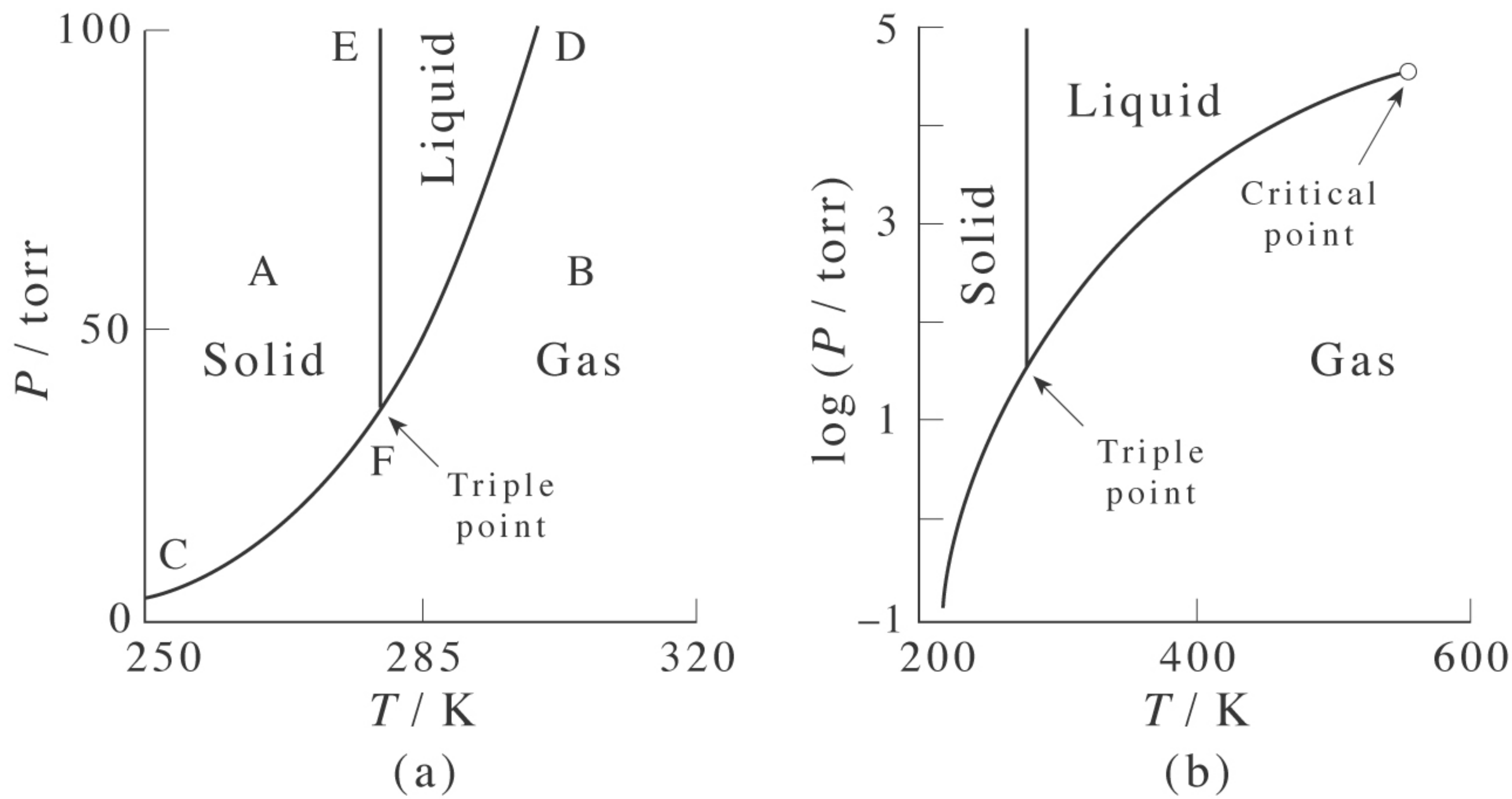


A phase diagram indicates the equilibrium phase of matter of a pure substance given specification of a pressure (*P*) and a temperature (*T*) "state point"

The "coexistence curves" in the phase diagram indicate the equilibrium co-existence of *multiple* phases

The triple point is the precise state point at which solid, liquid, and gas all *co-exist at equilibrium*

Alternative Benzene Phase Diagrams



Using log(P) in place of P often more convenient when a large temperature range is under consideration — note the effect on the curvature of the solid-gas and liquid-gas coexistence curves

Self-assessment

The vapor pressure above solid CO_2 can be described by the equation:

$$\ln(P/\mathrm{Pa}) = -\frac{3125}{T} + 27.58$$

And the vapor pressure above liquid CO_2 can be described by the equation:

$$\ln(P/\mathrm{Pa}) = -\frac{2011}{T} + 22.44$$

What is the temperature and pressure of a closed volume of CO_2 that contains solid, liquid, and gas at equilibrium? While this problem uses units of Pa — what is the pressure in atmospheres, also?

Self-assessment Explained

At the triple-point (all phases present), both vapor pressure equations must hold and give the same pressure, thus we can set them equal to one another and solve for $T_{\text{triple-point}}$:

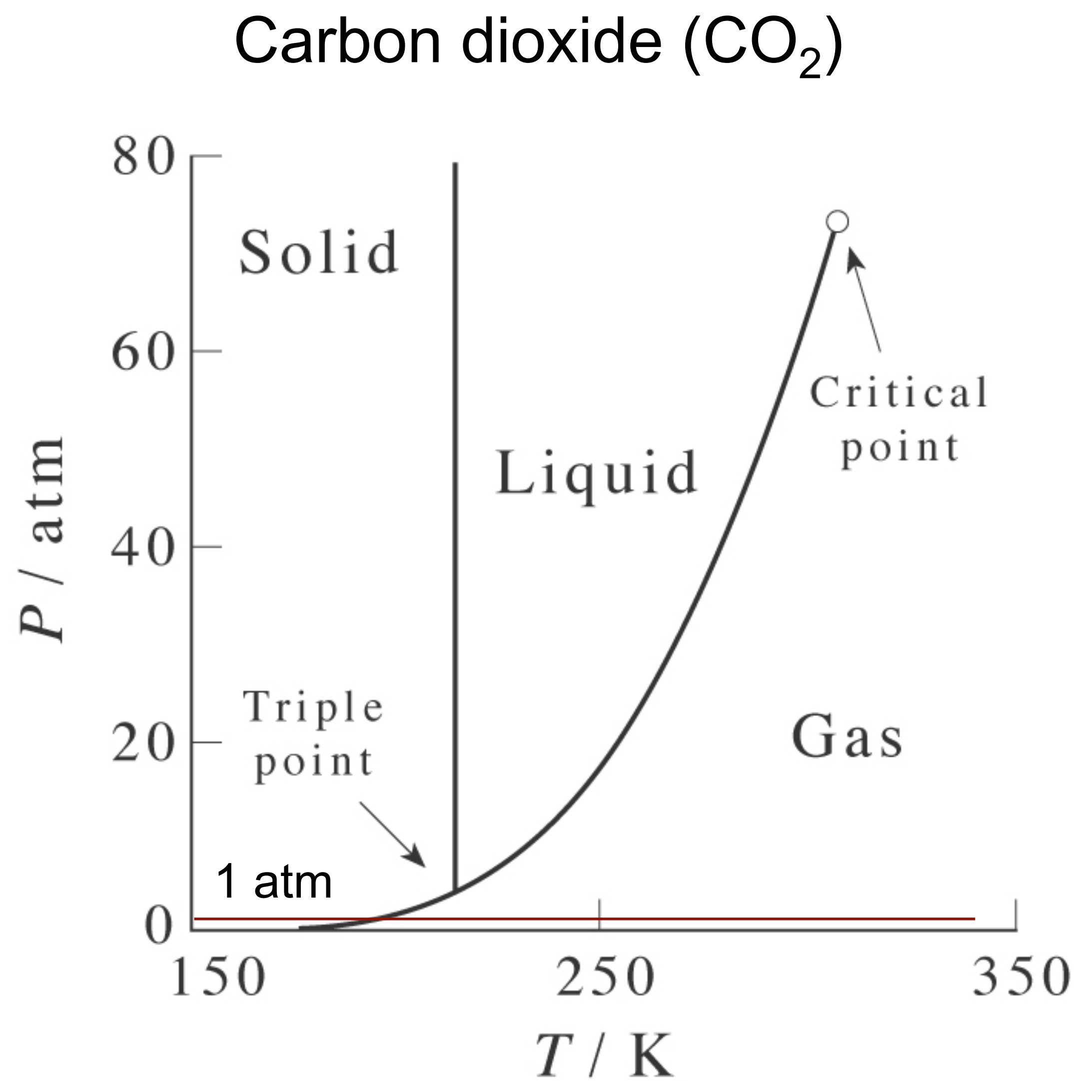
$$-\frac{3125}{T_{\text{triple-point}}} + 27.58 = -\frac{2011}{T_{\text{triple-point}}} + 22.44$$

Some quick algebra gives $T_{\text{triple-point}}$ = 216.73 K which, when plugged into either vapor pressure equation, permits computation of $P_{\text{triple-point}}$ = 519820 Pa, or about 5.1 atm.

(You can revisit the CO_2 triple-point demo and now you'll know the pressure inside the soda bottle!)

"Dry" Ice Sublimes Instead of Melting

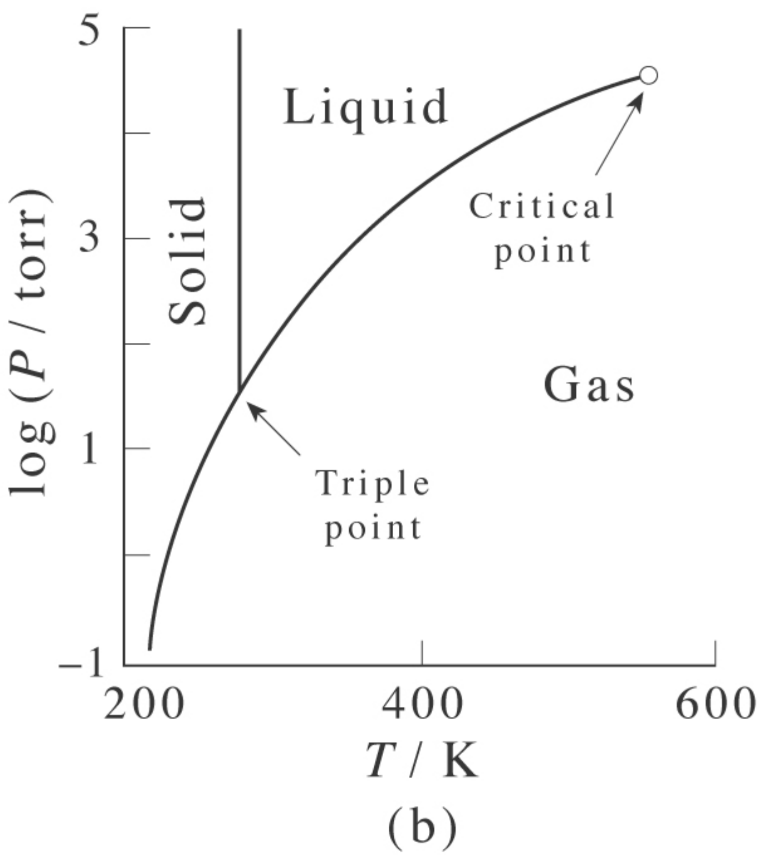
If 1 atm is *below* the triple point on a given phase diagram, the substance will sublime rather than melt at 1 atm (CO_2 triple point is 5.11 atm)



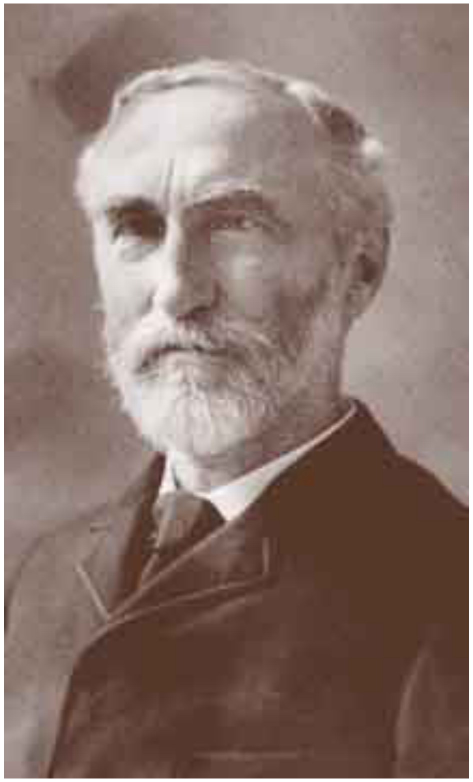
The Gibbs Phase Rule

$$f = 3 - p$$

f = "degrees of freedom" (P and/or T)
p = number of phases present (1, 2, or 3)

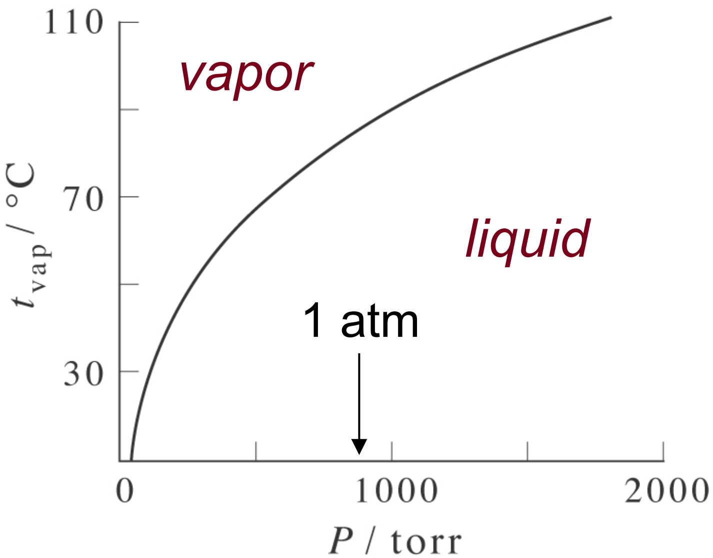


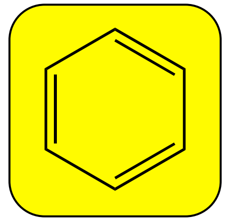
Note that the coexistence curves describe the pressure dependence of a <u>phase transition</u>

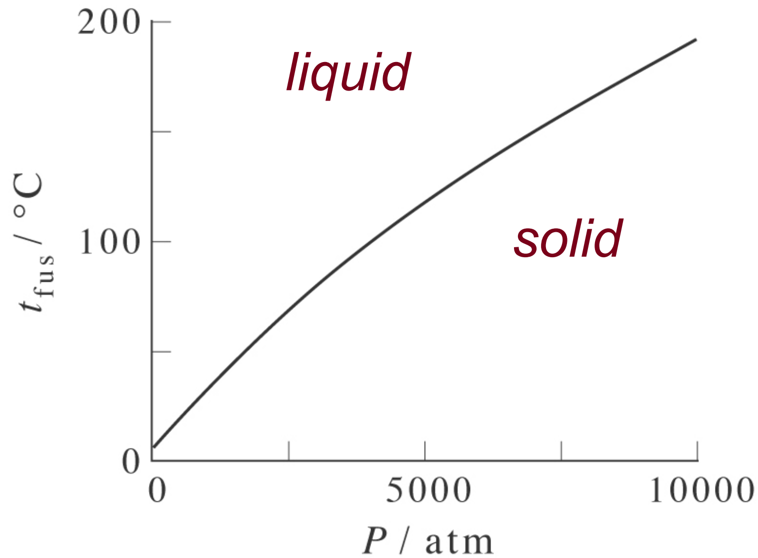


Josiah Williard Gibbs

Boiling and Melting as Function of *T*







Note different units of pressure

At 1 atm the boiling point is 80.1 °C
At 500 torr the boiling point is 67 °C

BP at 1 atm = *Normal boiling point*
BP at 1 bar = *Standard boiling point*

(1 torr = 1.33×10^{-3} bar = 1/760 atm)

At 1 atm the melting point is 5.5 °C (*normal*)
At 34 atm the melting point is 6.5 °C

slope ≈ 0.0293 °C • atm^{-1} (insensitive)

MP at 1 atm = *Normal melting point*
MP at 1 bar = *Standard melting point*

Next: Phase Diagram for Water