

STATISTICAL MOLECULAR THERMODYNAMICS

Christopher J. Cramer

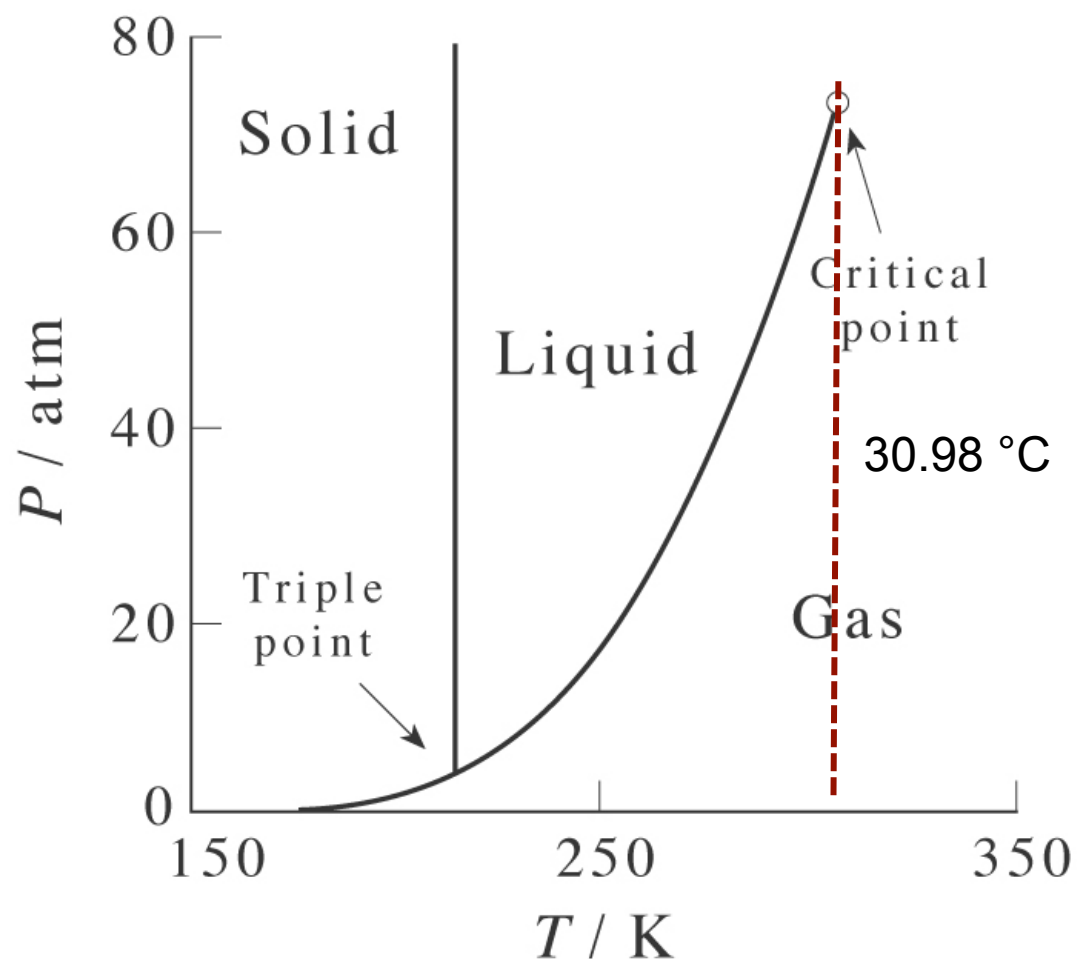
Video 9.3

Supercritical Behavior

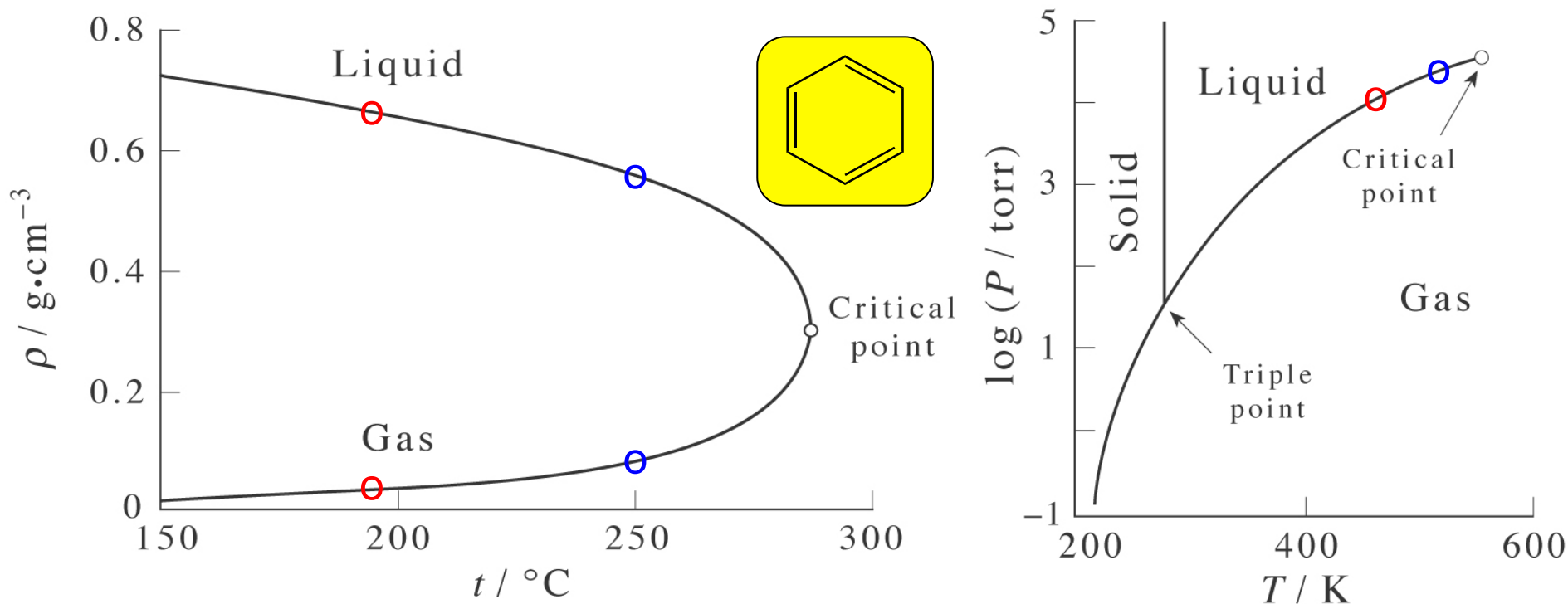
SUPERCRITICAL CARBON DIOXIDE

Carbon dioxide (CO₂)

Recall that the critical temperature is the temperature above which a gas cannot be liquefied irrespective of pressure (i.e., no phase change is observed with increasing pressure, although density will increase)

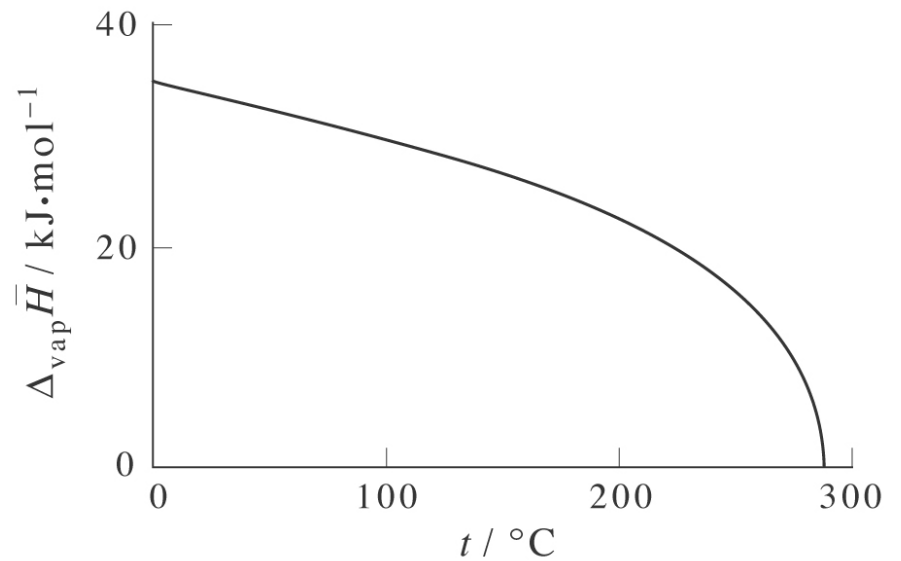
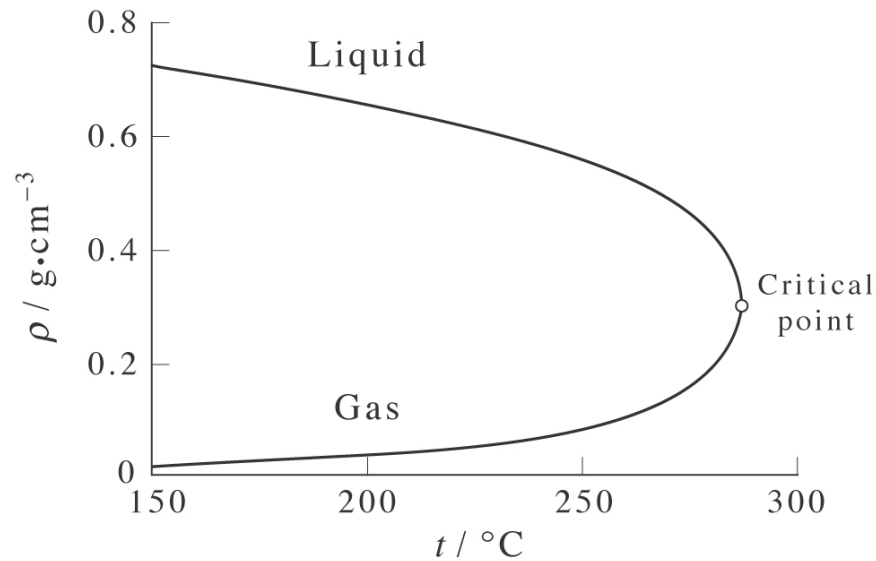


LIQUID AND GAS DENSITIES ALONG THE COEXISTENCE CURVE



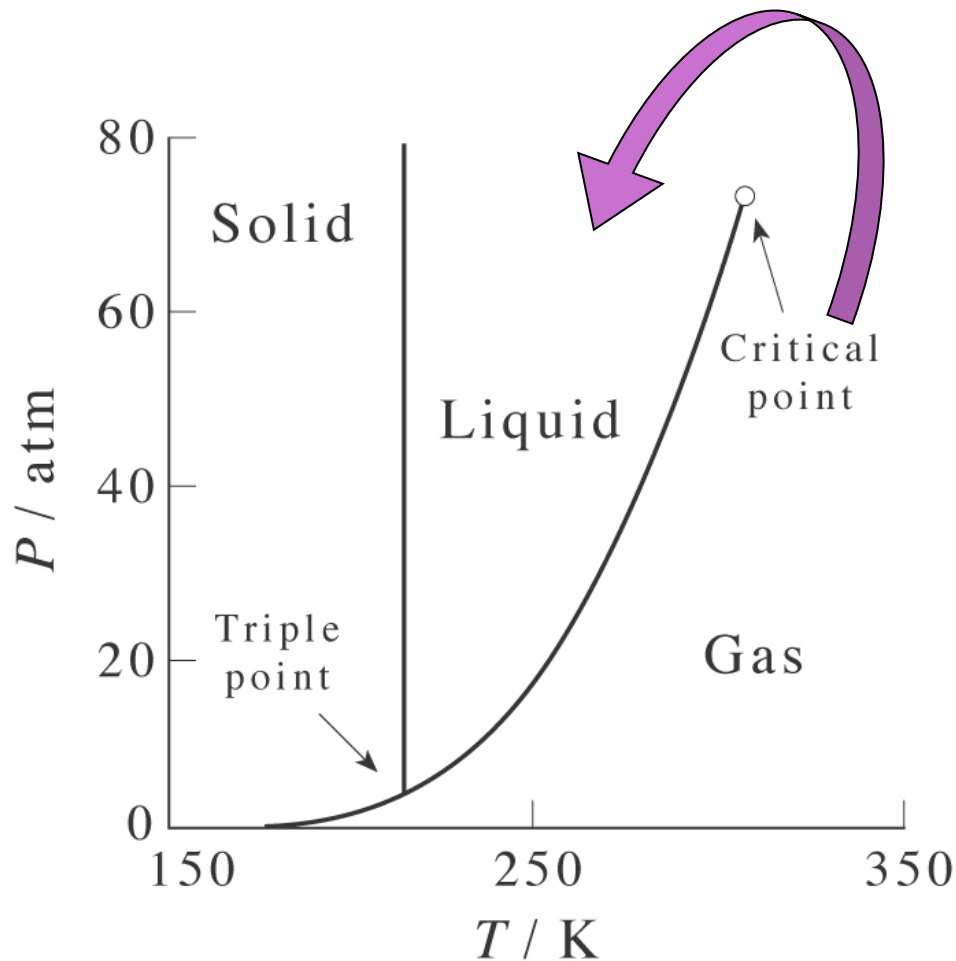
Orthobaric (both phases at identical pressures) densities of liquid and gas phases in equilibrium (i.e., on coexistence curve) as a function of temperature (only 1 degree of freedom allowed).

ENTHALPY OF VAPORIZATION AT T_c



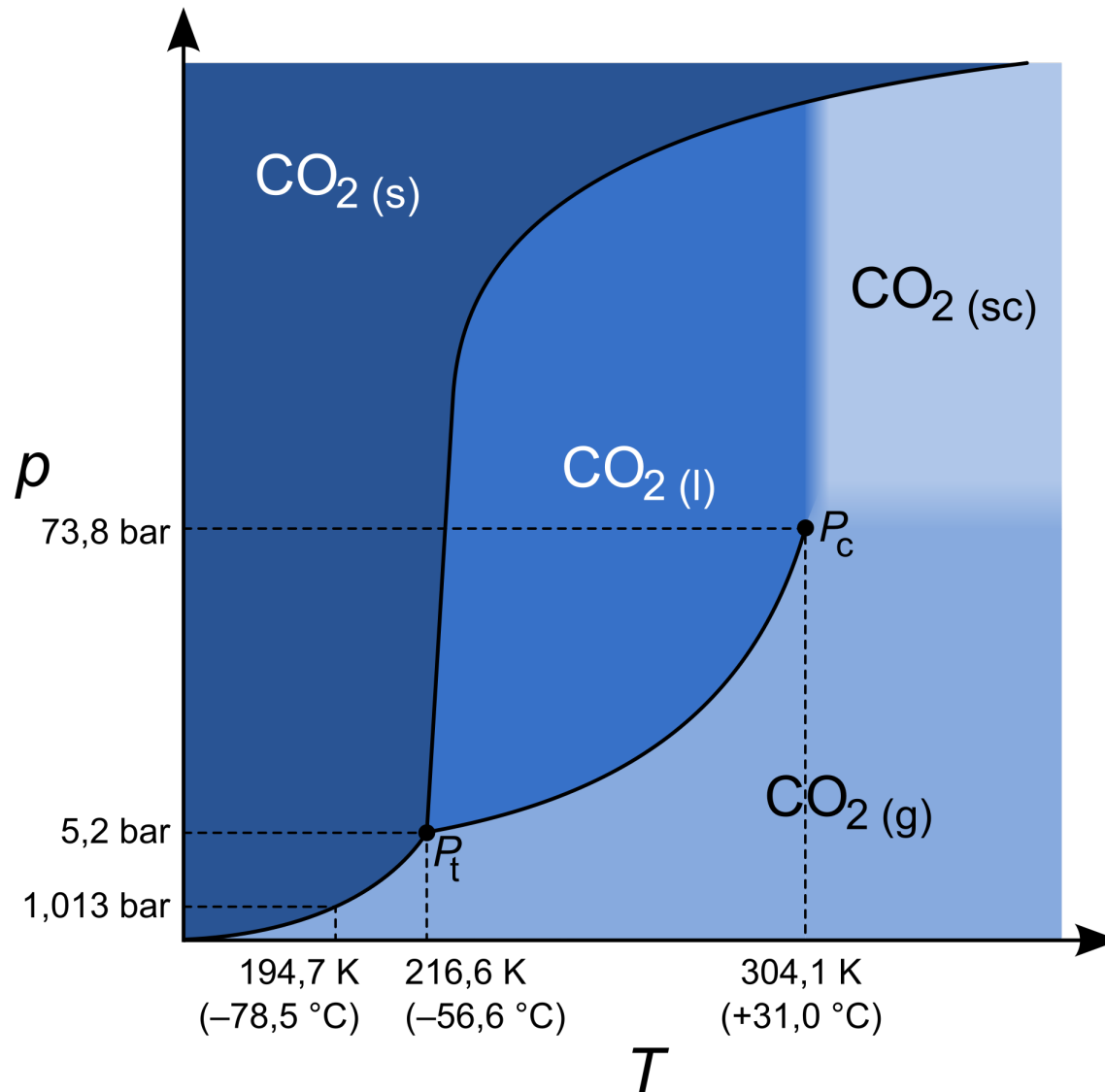
Molar enthalpy of vaporization goes to zero as critical temperature T_c is approached (i.e., no observable phase change, which is otherwise identified by observation of infinite heat capacity) — no longer need energy to “pull the molecules apart from one another”

SMOOTH LIQUID-GAS PHASE TRANSITION



By adjusting temperature and pressure (2 degrees of freedom) along the path of the purple arrow, the system will go from gas to liquid without ever passing through a state where two phases are simultaneously present

PHASE DIAGRAM — CARBON DIOXIDE



CARBON DIOXIDE DRY CLEANING!



Fluid CO₂ and a CO₂-soluble detergent can be used to clean clothing. Both the CO₂ and the detergent are recycled for repeated use!

The *chemist* who invented this process certainly took advantage of his knowledge of Thermodynamics!

Tuesday, February 4, 2003

1:25 PM - B75 Amundson

Professor Joseph M. DeSimone
Department of Chemistry, UNC
"The CO₂ Technology Platform"



also decaffeination (different machines...)

$$dU = \delta q + \delta w$$



Next: Phase Diagrams and Gibbs Free Energy