Statistical Molecular Thermodynamics

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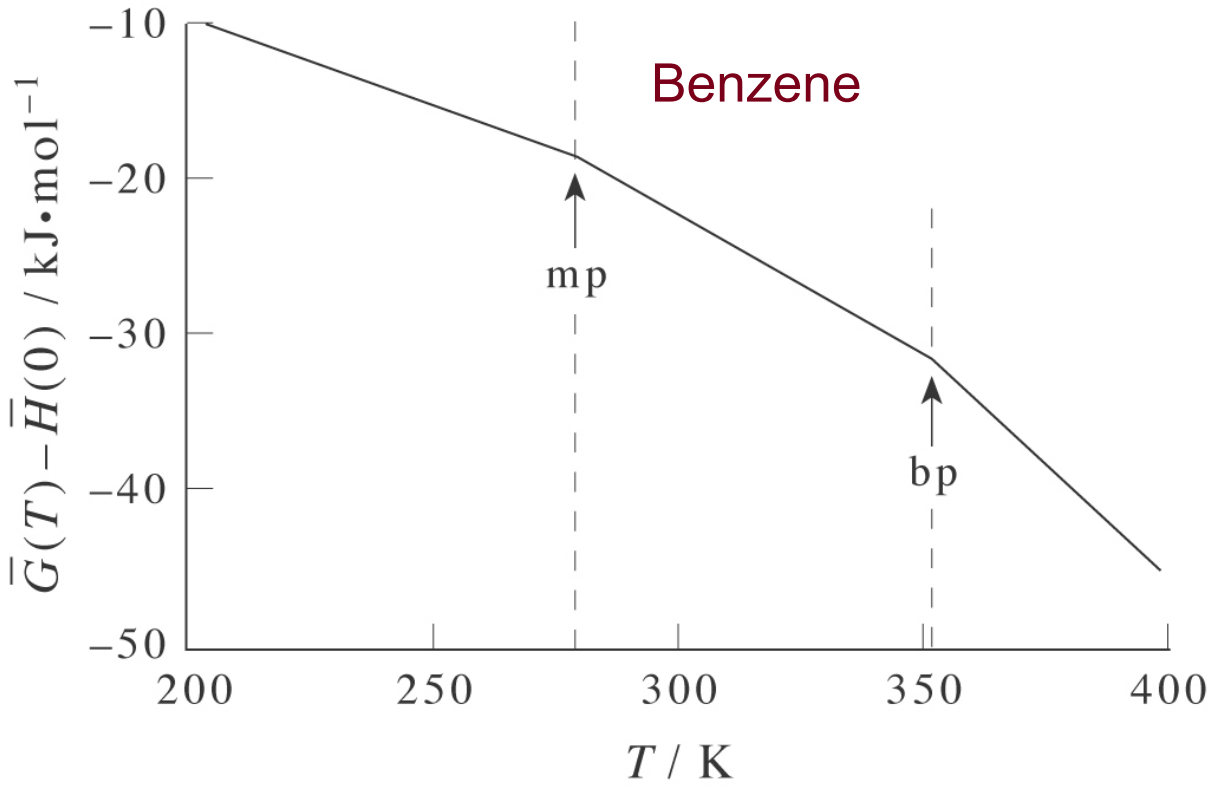
Video 9.4

Phase Diagrams and Gibbs Free Energy

Benzene Example Redux: G at 1 Bar

$$dG = -SdT + VdP$$

G decreases with increasing T



$$\overline{G}(T) - \overline{H}(0) = \overline{H}(T) - \overline{H}(0) - T\overline{S}(T)$$

Continuous at phase transitions since equilibrium implies same G

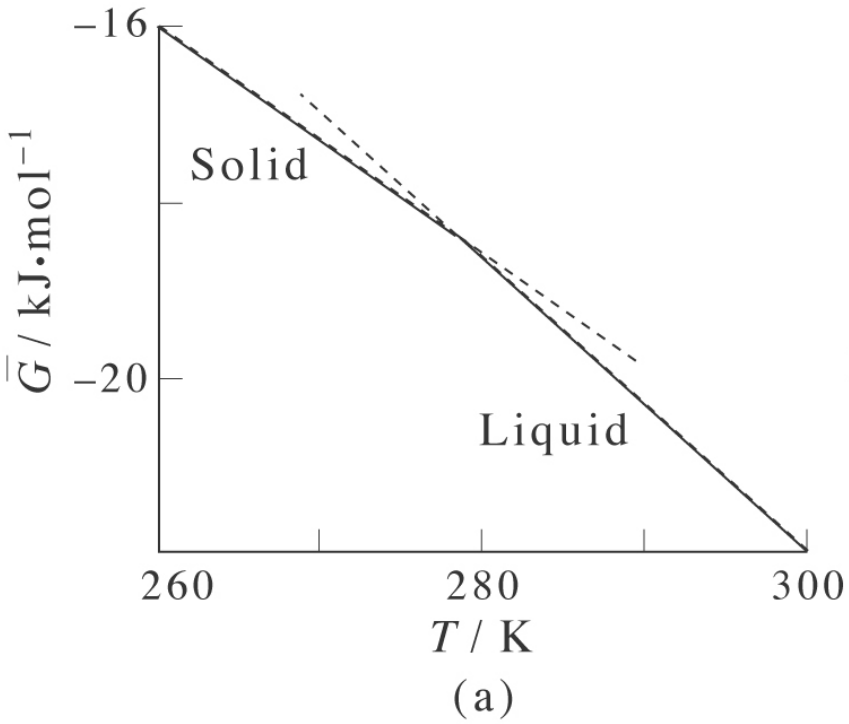
$$\Delta_{trs} G = 0$$

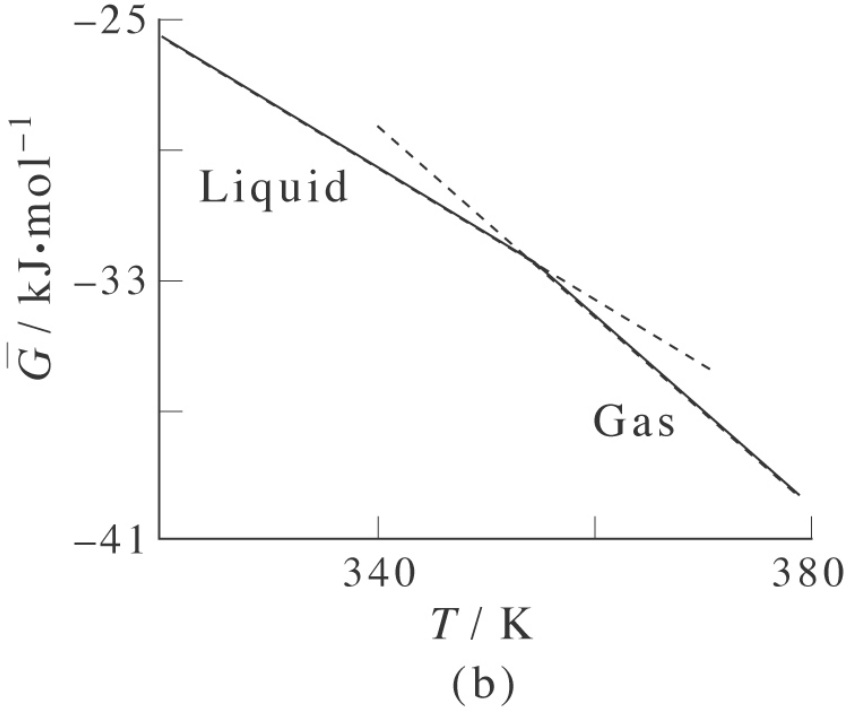
Discontinuous *slope* at phase transitions

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$S(\mathrm{g}) > S(\mathrm{l}) > S(\mathrm{s})$$

A Closer Look & Metastable Phases



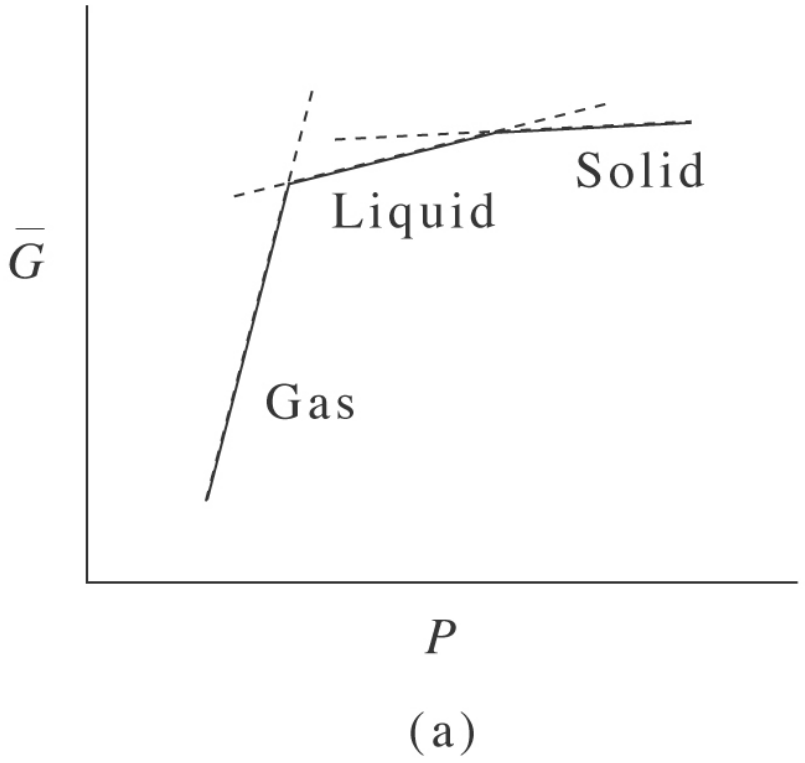


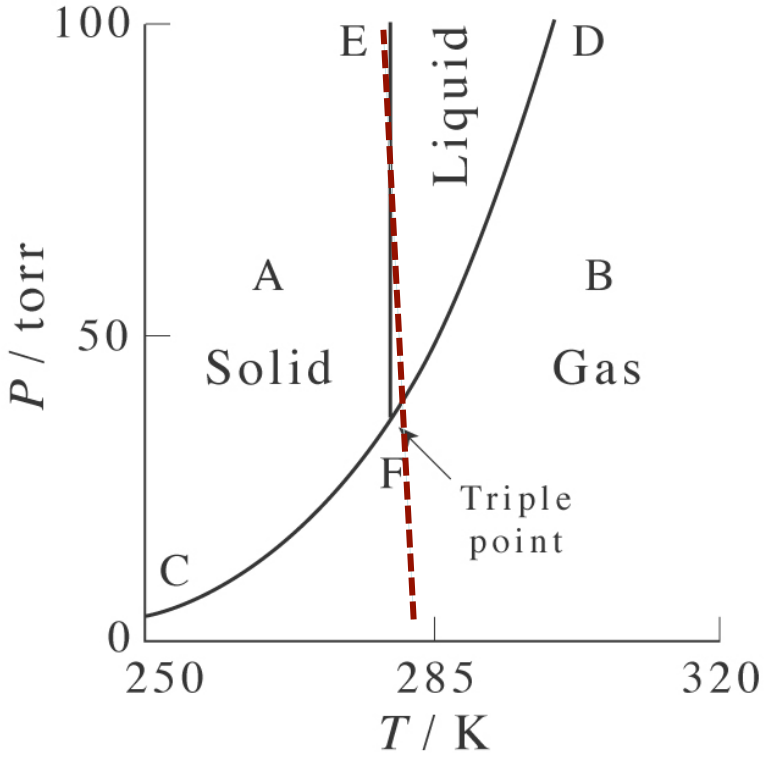
$$\left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S}^{\text{phase}}$$

- Continuous function
- Discontinuity in slope at each phase transition
- The slopes are related to the entropies of the phases
- The dashed lines are metastable states

What About Pressure Dependence?

benzene at *T* just *above* triple point

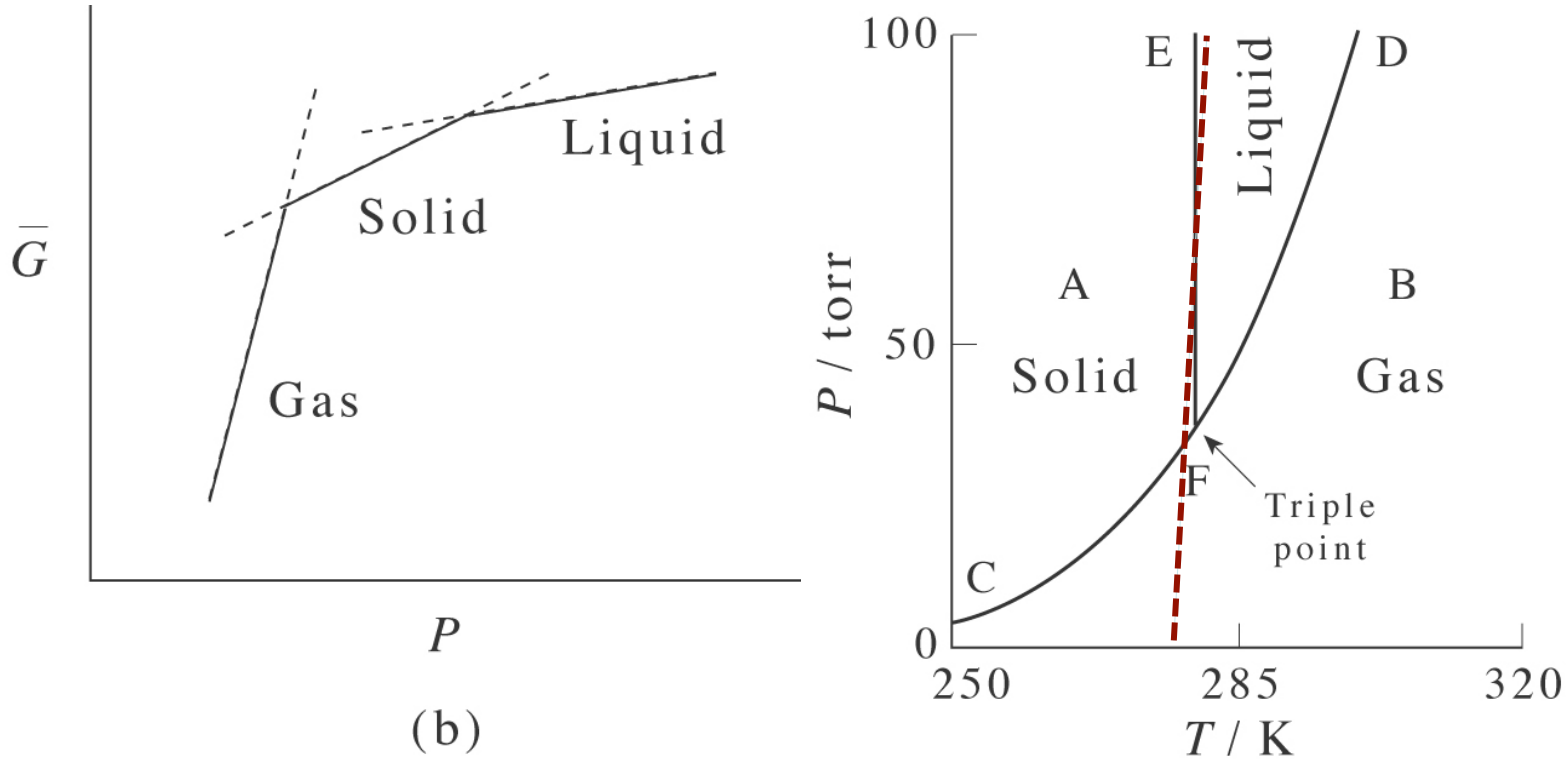




dashed line indicating chosen temperature on phase diagram should *be vertical, but is here slightly bent to emphasize crossing of both coexistence curves*

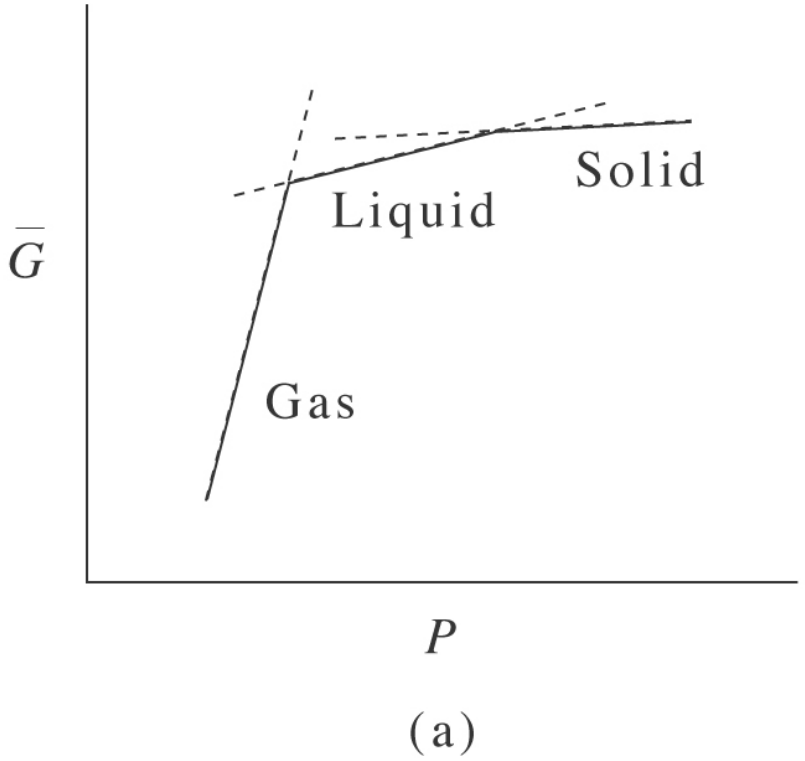
What About Pressure Dependence?

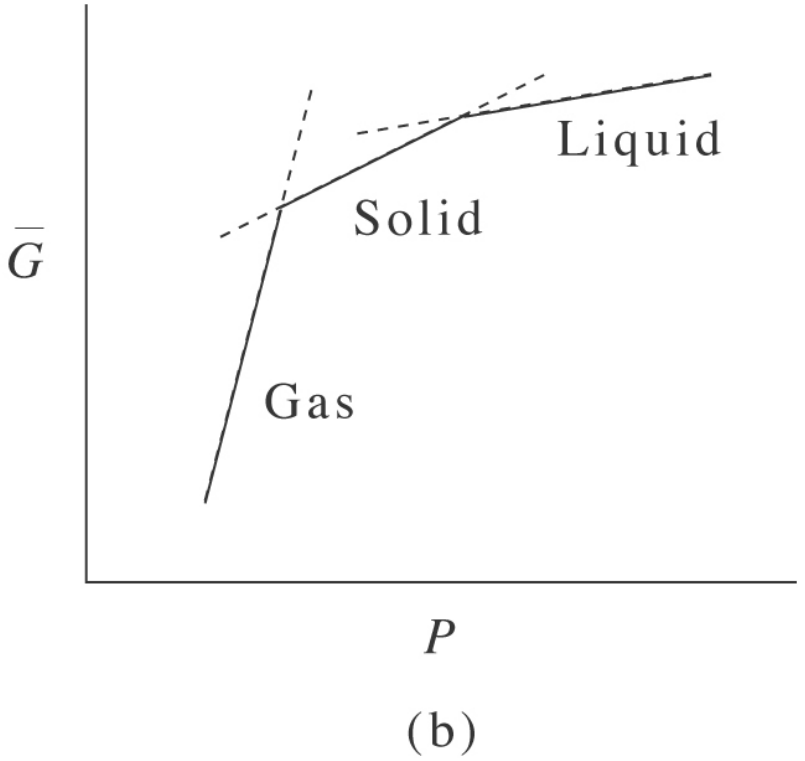
water at *T* just *below* triple point



dashed line indicating chosen temperature on phase diagram should *be vertical, but is here slightly bent to emphasize crossing of both coexistence curves*

Thermochemistry of P Dependence



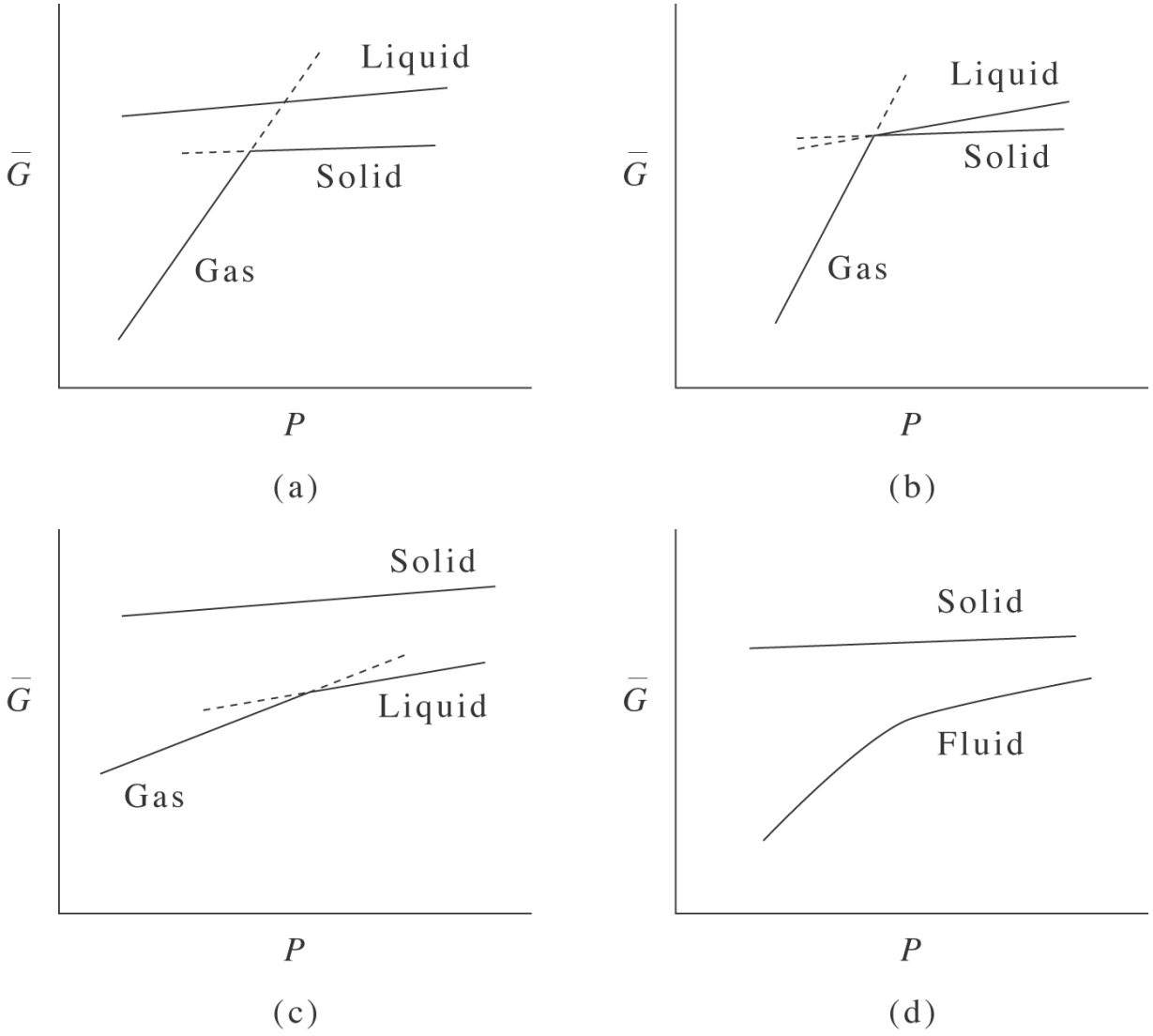


$$\left(\frac{\partial \bar{G}}{dP}\right)_T = \bar{V}^{\text{phase}}$$

- Always positive (so slopes are positive)
- Slope magnitudes depend on substance
- Construct from T-P phase diagrams ↑ P

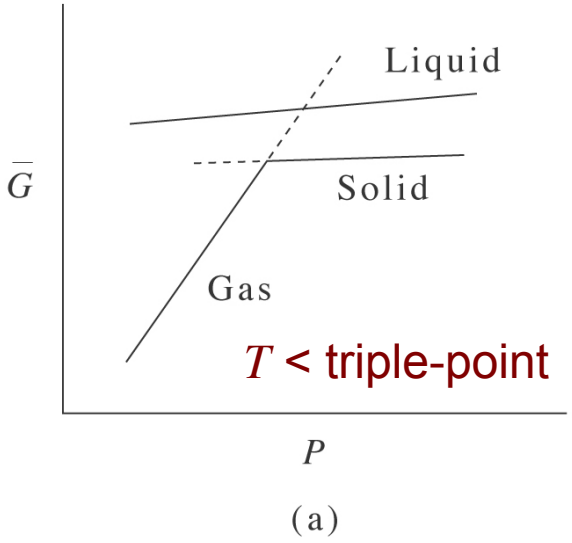
Self-assessment

For a substance with a solid state more dense than the liquid state, describe the temperatures in the pressure/free energy diagrams at right in relation to the triple-point temperature and/or the critical temperature

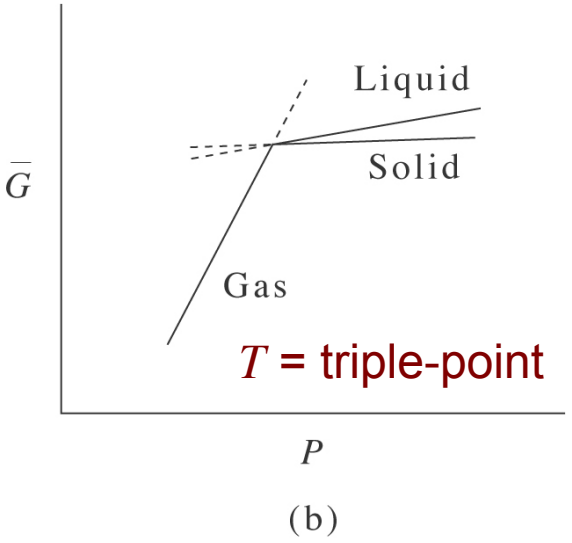


Self-assessment Explained

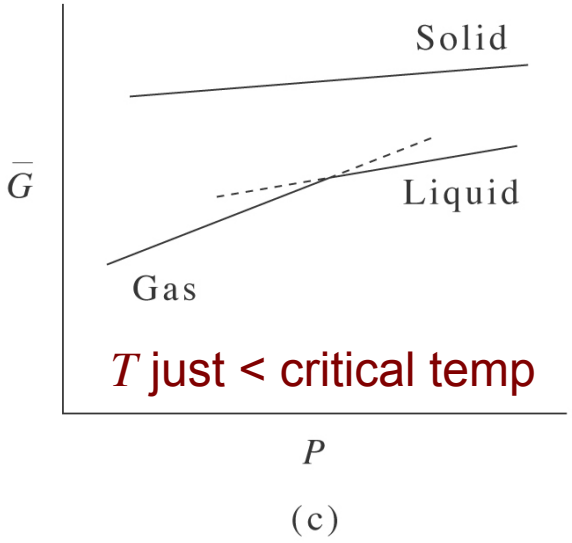
Use the benzene phase diagram and move the dashed brown pressure variation line to the indicated temperatures to convince yourself if the answers now labeling the various figures don't seem obvious to you



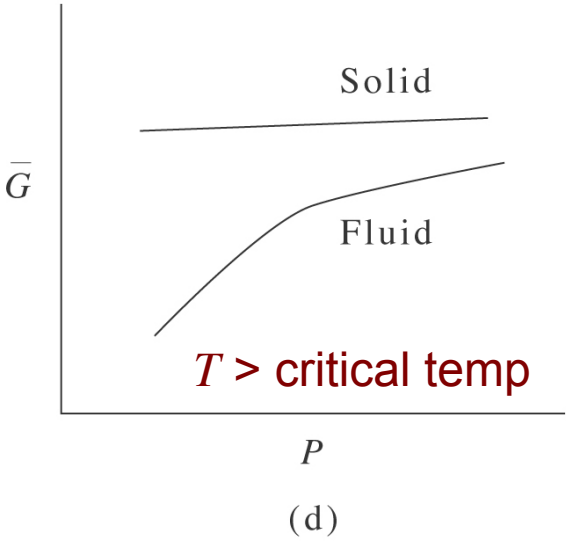
(a)



(b)



(c)



(d)

Next: Chemical Potentials and the Clapeyron Equation