

CHAPTER 5
THERMODYNAMICS: THE SECOND LAW
CHAPTER OUTLINE

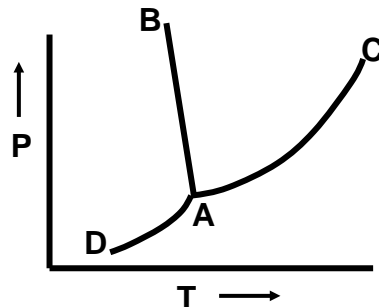
HW: Questions are below. Solutions are in separate file on the course web site.

Sect.	Material
1.	Vapor Pressure
2.	Phase Diagrams
3.	Heating Curves
4.	Quantitative Treatment of Phase Equilibrium
5.	Dependence of Gibbs Energy on Pressure
6.	Dependence of Reaction Gibbs Energy on Pressure: The Synthesis of Diamond

Chapter 5 - Homework

- 5.1 Consider the transition: $S(s, \text{rhombic}) \rightarrow S(s, \text{monoclinic})$.
 The standard molar entropy of rhombic sulfur is $31.80 \text{ J/mol}\cdot\text{K}$, and that of monoclinic sulfur is $32.60 \text{ J/mol}\cdot\text{K}$. The molar enthalpy change for this transition is $\Delta H_m = 568 \text{ J/mol}$.
- (a) Can an increase in temperature be expected to make monoclinic sulfur more stable than rhombic sulfur?
- (b) If so, at what temperature will the transition occur at 1 bar pressure?
- 5.2 The vapor pressure of liquid benzene [$M = 78$] is 17.7 kPa at $30 \text{ }^\circ\text{C}$ and 37.7 kPa at $50 \text{ }^\circ\text{C}$.
- (a) Calculate the Enthalpy of Vaporization of benzene
 (b) Estimate the vapor pressure at $10 \text{ }^\circ\text{C}$ [use your answer for part (a)].
 (c) Estimate the normal boiling point of benzene (the temperature at which the vapor pressure is 1 bar = 100 kPa) [use your answer for part (a)].
- 5.3 Use the data below to calculate q ($= \Delta H$, since $P = \text{constant}$) when $120. \text{ grams}$ of benzene gas at $120 \text{ }^\circ\text{C}$ is cooled (at constant pressure) to solid benzene at $-20 \text{ }^\circ\text{C}$.
- | | | |
|---|--|--|
| $T_{\text{bo}} = 80 \text{ }^\circ\text{C}$ | $\Delta_{\text{vap}}H^\circ = 30.8 \text{ kJ/mol}$ | $C_{P,m}(\text{gas}) = 81.7 \text{ J/mol}\cdot\text{K}$ |
| $T_{\text{mo}} = 6 \text{ }^\circ\text{C}$ | $\Delta_{\text{fus}}H^\circ = 9.9 \text{ kJ/mol}$ | $C_{P,m}(\text{liq}) = 136.1 \text{ J/mol}\cdot\text{K}$ |
| $C_{P,m}(\text{sol}) = 61.2 \text{ J/mol}\cdot\text{K}$ | | |
- 5.4 A solid has two crystalline phases, $A(s)$ and $B(s)$. For the transition $A(s) \rightarrow B(s)$, $\Delta G^\circ = +6.0 \text{ kJ/mol}$ (i.e. at 1 bar pressure). The molar volumes of the two phases are $V_m(A) = 23.8 \text{ mL/mol}$ and $V_m(B) = 17.2 \text{ mL/mol}$. At what pressure (in bar) are the two phases in equilibrium?

- 5.5 Consider the phase diagram to the right.



- (a) The Triple Point in the diagram is represented by
- (A) Point A (B) Point B (C) Point C (D) Point D

- (b) The slope of curve A-B is negative because
(A) $S_m(\text{liq}) > S_m(\text{sol})$ (B) $S_m(\text{liq}) < S_m(\text{sol})$ (C) $V_m(\text{liq}) > V_m(\text{sol})$
(D) $V_m(\text{liq}) < V_m(\text{sol})$
- (c) The magnitude of the slope of curve A-B is greater than the magnitude of the slope of curve A-C because:
(A) $|\Delta V_{\text{fus}}| < |\Delta V_{\text{vap}}|$ (B) $|\Delta V_{\text{fus}}| > |\Delta V_{\text{vap}}|$ (C) $\Delta S_{\text{fus}} < \Delta S_{\text{vap}}$
(D) $\Delta S_{\text{fus}} > \Delta S_{\text{vap}}$
- (d) The slope of curve A-D is greater than the slope of curve A-C because:
(A) $\Delta V_{\text{sub}} < \Delta V_{\text{vap}}$ (B) $\Delta V_{\text{sub}} > \Delta V_{\text{vap}}$ (C) $\Delta S_{\text{sub}} < \Delta S_{\text{vap}}$
(D) $\Delta S_{\text{sub}} > \Delta S_{\text{vap}}$
- (e) If the pressure on this substance is increased from 1. bar to 10 bar, the boiling point temperature will
(A) Decrease (B) Increase (C) Remain the same
(D) Increase or decrease depending on the relative liquid and vapor entropies
- (f) If the pressure on this substance is increased from 1. bar to 500 bar, the melting point temperature will
(A) Decrease (B) Increase (C) Remain the same
(D) Increase or decrease depending on the relative liquid and solid entropies