

Problem Set PS09

ISSUED: 3/23/99 Due: 3/30/00

Prof. Darin J. Ulness

Name _____

Instructions. Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

Exercises

1. Derive every equation in the table on page 112 of the notes.
2. Express the equation of state for internal energy and entropy for a van der Waals gas at constant volume. (The working equation for dU and dS you derived above)
3. Express the equation of state for internal energy and entropy for a Berthelot gas.
4. Five moles of an ideal gas (molar heat capacity: $C_m = 20.0 \text{ J/(K mol)}$) at 300K is contained in a piston under 1.00atm. A scientist jumps on the piston as shown below to cause adiabatic compression under a constant pressure of 3.00atm. The new volume is 100L. What are ΔT , ΔU , and ΔS for this process?
5. Derive an expression for $d\mu(T, V)$ that is analogous to the last line of Eq. (18.13) by starting with the Helmholtz free energy version of Eq. (18.8).
6. Derive a Clapeyron like equation using your result from the previous problem.

Conceptual Problems

7. Explain the law of corresponding states.
8. In the notes we say “a diamond is not forever.” Why is “a diamond is forever” a reasonable slogan for the diamond industry.
9. Figure 5.1 on page 187 of Laidler and Meiser show a phase diagram for water. Water is an unusual substance. Pretend water is a usual substance and draw the new phase diagram. How is it qualitatively different from the real phase diagram?

10. In the figure below identify (i) the phases in regions A B and C (ii) the processes a, b, and c, and (iii) the points 1 and 2.

① see last semester's work

$$dU = C_v dT + \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV$$

$$P = \frac{nRT}{V-nb} - \frac{n^2 a}{V^2} \quad \left(\frac{\partial P}{\partial T} \right)_V = \frac{nR}{V-nb}$$

$$dU = C_v dT + \left[T \frac{nR}{V-nb} - \frac{nRT}{V-nb} + \frac{n^2 a}{V^2} \right] dV$$

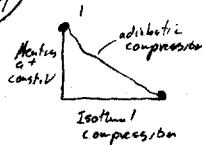
$$dU = C_v dT + \frac{n^2 a}{V^2} dV$$

③ $P = \frac{nRT}{V-nb} - \frac{n^2 a}{TV^2} \quad \left(\frac{\partial P}{\partial T} \right)_V = \frac{nR}{V-nb} + \frac{n^2 a^2}{TV^2}$

$$dU = C_v dT + \left[T \left(\frac{nR}{V-nb} + \frac{n^2 a^2}{TV^2} \right) - \frac{nRT}{V-nb} + \frac{n^2 a^2}{TV^2} \right] dV$$

$$dU = C_v dT + 2 \frac{n^2 a^2}{TV^2} dV$$

④



$T_1 = 300K$
 $V_1 = ?$
 $P_1 = P_2 = P_{ext} = 3.0 \text{ atm}$
 $T_2 = ?$
 $V_2 = 100L$
 $P_0 = 1 \text{ atm}$

$$V_1 = \frac{nRT}{P_0} = \frac{(5)(0.0821 \text{ atm})(300K)}{1 \text{ atm}} = 123L$$

adiabatic so $\Delta U = \Delta H + W = -P_{ext} \Delta V = -3.0(100-123) = 69 \text{ cal}$
 $\Delta U = 6990J$

$$\Delta T = \frac{\Delta U}{nC_m} = \frac{6900J}{5(200 \frac{J}{K})} = 70K$$

$$\Delta S = \Delta S_{isothermal} + \Delta S_{heating} = nR \ln \frac{V_2}{V_1} + nC_v \ln \frac{T_2}{T_1}$$

$$= 5(8.314) \ln \frac{100}{123} + 5(20) \ln \frac{370}{300} = 12.37 \frac{J}{K}$$

⑤ $dA = -SdT - PdV + \mu dn$

$$S = - \left(\frac{\partial A}{\partial T} \right)_{P, n}$$

$$\frac{\partial S}{\partial n} = - \frac{\partial}{\partial n} \left(\frac{\partial A}{\partial T} \right) = - \frac{\partial^2 A}{\partial T \partial n} = - \frac{\partial \mu}{\partial T}$$

but $\frac{\partial \mu}{\partial n} = S_m$ so $-\frac{\partial \mu}{\partial T} = S_m$ multiply $\frac{\partial \mu}{\partial V_m} = -P$

$$d\mu(T, V) = \left(\frac{\partial \mu}{\partial T} \right) dT + \left(\frac{\partial \mu}{\partial V} \right) dV_m$$

$$d\mu = -S_m dT - P dV_m$$

⑥ $\mu_A = \mu_B \Rightarrow d\mu_A = d\mu_B$

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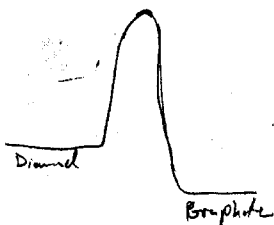
$$-S_m dT - P dV_m = -S_{mB} dT - P dV_{mB}$$

$$\frac{dV_m}{dT} = \frac{S_{mA} - S_{mB}}{-(V_{mA} - V_{mB})} = \frac{-\Delta S_m}{\Delta V_m} = \frac{-\Delta G_m}{T \Delta V_m}$$

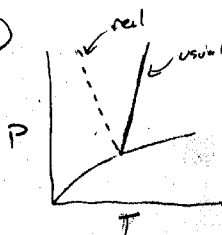
$$\frac{dV_m}{dT} = \frac{-\Delta G_m}{T \Delta V_m}$$

⑦ your words

⑧ The kinetic barrier for the diamond \rightarrow graphite phase transition is very high that is,



⑨



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⑩

- A: solid
- B: liquid
- C: gas

- a: opposite of sublimation
- b: melting
- c: evaporation