CYL100 2013–14 I semester Homework 1

Handed out: July 29, 2013 Due in: August 2, 2013

1. Dieterici's equation of state for a gas is $P(V-b)\exp(a/RVT) = RT$, where a, b, and R are constants. Determine $(\partial V/\partial T)$, $(\partial T/\partial P)$, and $(\partial P/\partial V)$ and verify that $(\partial V/\partial T)\ (\partial T/\partial P)\ (\partial P/\partial V) = -1$.

2. Given the equation of state $V = V_0(1+\alpha T-\beta P)$ for a liquid where V_0, α, and β are constants: (a) Derive an expression for the work done when the pressure on the liquid is increased reversibly and isothermally from P_1 to P_2. (b) Use your equation to evaluate the work done when 2.00 mol of water ($\beta = 4.67\times10^{-5}$ atm^{-1}) is subjected to an increase in pressure from 1.00 atm to 2.00 atm at 25 °C.

3. When you open a can of your favorite aerated drink, compressed CO_2 expands irreversibly against the atmosphere as it bubbles up through the drink. Assume that the process is adiabatic and that the CO_2 has an initial pressure of 3 bar. Take CO_2 to be an ideal gas, with a constant heat capacity of $C_P = 37$ J/(mol K). What is the final temperature of the CO_2 after it has reached atmospheric pressure?

4. Consider a piston-cylinder assembly that contains 1 mole of ideal gas A. The system is well insulated. Its initial volume is 10 L and initial pressure, 2 bar. The gas is allowed to expand against a constant external pressure of 1 bar until it rteaches mechanical equilibrium. Is this a reversible process? What is the final temperature of the system? How much work was obtained? For gas A $C_V = 5/2R$.

5. For the well-insulated piston-cylinder assembly containing 1 mole of ideal gas described in the previous problem, describe the process by which you can obtain the maximum work from the system. Calculate the value for the work. What is the final temperature? Explain the difference, if any, in the final temperature of the gas in this problem and the previous one.

6. At high densities the molecules themselves make up an appreciable fraction of the available volume, and an equation of state of 1 mol of gas can be written in the form $P(V-b) = RT$, where 'b' is a constant which is related to the size of the molecules. (i) Calculate the work done when 1 mole of this nonideal gas at 298 K is compressed reversibly and isothermally from 22.4 L to 0.224 L if 'b' is 0.04L. (ii) What is the work done if the gas behaves ideally in (i) and explain why the answers differ in (i) and (ii).

7. For each of the following processes deduce whether each of the quantities q, w, ΔU, ΔH is positive, zero, or negative. (a) Reversible melting of solid benzene at 1 atm and the normal melting point. (b) Reversible melting of ice at 1 atm and 0°C. (c) Reversible adiabatic expansion of a perfect gas. (d) Reversible isothermal expansion of a perfect gas. (e) Adiabatic expansion of a perfect gas into a vacuum. (f) Reversible heating of a perfect gas at constant P. (g) Reversible cooling of a perfect gas at constant V.

8. The isothermal compressibility of lead is 2.3×10^{-6} atm^{-1}. A cube of lead of 10 cm length at 298K is inserted under 1000m of water where the temperature is 268K. Calculate the change in the volume of the cube given that the mean density of water is 1.03 g cm^{-3} and α_{Pb} is 8.61×10^{-5}.

9. The molar heat capacity of oxygen at constant pressure for temperatures in the range 300 to 400 K and for low or moderate pressures can be approximated as C_P(J mol^{-1} K^{-1}) = 25.73 + 0.013 T. (a) Calculate q, w, ΔU, ΔH when 2 mol of O_2 is reversibly heated from 27 to 127 °C with P held fixed at 1 atm. (b) Repeat the calculation if the same change is effected at constant V.

10. Read the following statements *carefully* and decide whether (and why) they are true or false giving your thermodynamic reasoning. If the statement is false, you may either state which law or laws of thermodynamics it violates or provide a physical counter example or any other plausible physical reason. Finally, correct the false statement with a clarifying phrase that makes the statement true.
(i) The internal energy of a system and its surroundings is not conserved during an irreversible process, but it is conserved for reversible processes.
(ii) No heat transfer occurs when liquid water is reversibly and isothermally compressed.
(iii) If in a reversible process the temperature of one mole of an ideal gas increases by 1°C, the work done on the gas must be numerically equal to the molar heat capacity at constant volume, C_V.
(iv) If an ideal gas increases its volume by 1 cubic meter at a constant pressure of 1 Newton per square meter, then its internal energy decreases by 1 Joule.
(v) Melting of any material is an endothermic process.