SHOW ALL WORK/EXPLAIN YOUR ANSWERS FOR FULL CREDIT

Possibly useful relations:

 $k_B = 1.3807 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}; R \text{ (molar gas constant)} = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ $\ln(1+x) = x - x^2/2 + \dots$ $(1+x)^{-1} = 1 - x + x^2 + \dots$

- 1. One mole of a monatomic ideal gas initially at a pressure of P_1 , volume V_1 , and a temperature of T_1 is subjected to an external pressure of $P_2 = 2P_1$ and compressed isothermally. Give expressions, in terms of V_1 , and/or T_1 for the following quantitites:
 - a. ΔU ? (5 pts) For an ideal gas $dU = C_V dT$ (energy depends only on the temperature). For an isothermal process dT = 0, thus $\Delta U = 0$
 - b. q? (10 pts). By the 1st law, $q = \Delta U w$. Here, $\Delta U = 0$, and $w = \int \delta w = -\int P dV$. In compression, work is generated by application of an external pressure to the system. Here, the external pressure is constant at $P = P_2$ (an irreversible compression) Thus $w = -P_2\Delta V = P_2(V_2 - V_1)$. Since $P_2 = 2P_1$, $V_2 = V_1/2$, so $w = P_2V_1/2$. Thus $q = -w = -P_1V_1$
- 2. One mole of a monatomic ideal gas initially at a pressure of P_1 and a temperature of T_1 is taken to a final pressure of $P_2 = 2P_1$ by the reversible path defined by $PV^{-1/2} = C$, where C is a constant. Plot P/P_1 as a function of V/V_1 over the range $0.5 \le V/V_1 \le 4$. (10 pts) Since $PV^{-1/2}=C$, it follows that $P1V^{-1/2} = P_1V_1^{-1/2}$ or $P/P_1 = (V/V_1))^{1/2}$



3. The equation of state of a van der Waals gas is

$$P = \frac{RT}{(\bar{V} - b)} - \frac{a}{\bar{V}^2}$$

- a. One mole of a van der Waals's gas is at T_1, P_1 . The gas expands at constant volume (isochorically) from T_1 to T_2 . Determine, for this transformation, expressions in terms of R, T_1, T_2, V_1, a , and b for
 - i. ΔP (5 pts)

$$\Delta P = P_2 - P_1 = \frac{RT_2}{(\bar{V}_2 - b)} - \frac{a}{\bar{V}_2^2} - \left[\frac{RT_1}{(\bar{V}_1 - b)} - \frac{a}{\bar{V}_1^2}\right]$$

Since the volume is constant, the two terms in V^{-2} cancel, and we have

$$\Delta P = R(T_2 - T_1) \frac{1}{\bar{V}_1 - b}$$

- ii. w (5 pts) we know that $\delta w = -PdV$. For an isochoric expansion, dV = 0, hence w = 0.
- b. In chapter 8, we will derive the formula

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \tag{1}$$

One mole of a van der waals gas expands isothermally from V_1 to V_2 . Determine an expression for ΔU for this transformation. (10 pts) From Eq. (1) for a van der Waal's

gas we have

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{R}{\bar{V}-b} - P = \frac{RT}{\bar{V}-b} - \left[\frac{RT}{(\bar{V}-b)} - \frac{a}{\bar{V}^2}\right] = \frac{a}{\bar{V}^2}$$

Integration gives

$$\Delta U = \int \frac{\partial U}{\partial V_T} dV = -\left. \frac{a}{\bar{V}} \right|_{V_1}^{V_2} = a \left[\frac{1}{\bar{V}_1} - \frac{1}{\bar{V}_2} \right]$$

4. One mole of a monatomic ideal gas at temperature T_1 is confined in a volume V_1 and



isolated from the surroundings. The partition is removed and gas allowed to expand into the vacuum. The final volume is $V_2 = 3V_1$. Determine expressions, in terms of R, V_1 and T_1 for the following quantitites:

- a. w. No work is done, w = 0
- b. q Isolated system, hence q = 0.
- c. T_2 (5 pts) Here q = 0 (since the system is isolated. Also, no work is done, so from the first law $\Delta U = 0$. For an ideal gas the energy depends only on the temperature $[(\partial U/\partial V)_T = 0]$. Thus, since $\Delta U = 0$, the temperature is unchanged. $T_2 = T_1$ You could also say that for an ideal gas $dU = C_V dT$ or $\Delta U = C_V \Delta T$. Since C_V is not zero, and since $\Delta U = 0$, it follows that $\Delta T = 0$ so that $T_2 = T_1$.
- d. ΔS (10 pts) (Your answer should be in terms of only R) The transformation is not reversible, hence ΔS is not given by $\int \delta q/T = 0$. However, ΔS can be derived from consideration of a process which takes us, reversibly, from the same initial state to the same final state . This is an isothermal (since T doesn't change) expansion, of an ideal gas from V_1 to V_2 . We know for an isothermal expansion of one mole of an ideal gas dS = RdV/V, or $\Delta S = R \ln V_2/V_1 = R \ln 3$

- 5. a. For a constant pressure transformation with no phase change involved, derive the relation between dS and C_P . (10 pts) We know that $dS = \delta q_{rev}/T$. At constant pressure $\delta q_{rev} = dH$. Also, $dH = (\partial H/\partial T)_V dT + (\partial H/\partial P)_T dP$. The first partial derivative is denoted C_P and at constant pressure the second term equals zero, so that $dH_P = C_P dT$ (the constant pressure transformation involves only a change in temperature.) Thus $dS = (C_P/T)dT$
 - b. One mole of ethane at temperature T_1 is heated to T_2 at constant pressure. Over this range, the heat capacity of ethane can be expressed as

$$\bar{C}_P/R = A + BT + CT^2$$

determine ΔS for this transformation in terms of T_2 , T_1 and the constants A, B, and C, (10 pts) From part (a): that $\Delta S = \int_i^f \delta q_{rev}/T$. At constant pressure $\delta q_{rev} = dH$. Also, $dH = (\partial H/\partial T)_V dT + (\partial H/\partial P)_T dP$. The first derivative is named C_P and at constant pressure the second term equals zero, so that, here, $dH_P = C_P dT$. Thus

$$\Delta S = \int_{T_1}^{T_2} \delta q_{rev} / T = \int_{T_1}^{T_2} C_P \frac{dT}{T}$$

(You could start with this equation for full credit). Insertion of the expression for \bar{C}_P gives, for one mole,

$$\Delta S = \int_{T_1}^{T_2} \frac{1}{T} (A + BT + CT^2) dT = \int_{T_1}^{T_2} (A/T + B + CT) dT$$
$$= \left[A \ln T + BT + \frac{1}{2} CT^2 \right]_{T_1}^{T_2} = A \ln(T_2/T_1) + B(T_2 - T_1) + \frac{1}{2} C(T_2^2 - T_1^2)$$

6. A two-level system has energy levels $-\varepsilon$ and ε , where ε is a positive number. The upper level is doubly degenerate. In terms of the variable $x = \exp(-\varepsilon\beta) = \exp(-\varepsilon/k_B T)$ the partition function and average energy are given by

$$q = 1/x + 2x = (1 + 2x^2)/x$$
 and $\langle E \rangle = \frac{2x^2 - 1}{2x^2 + 1}\varepsilon$

The entropy is defined as

$$S = \frac{\langle E \rangle}{T} + k_B \ln q$$

What is the high temperature limit of the entropy? (10 pts) At high temperature $x \to 1$

and the $\langle E \rangle / T$ term goes to zero, so $\lim_{T \to \infty} S = k \ln 3$. You could also say that at high temperature $\Omega = 3$, so that $S = k \ln \Omega = k \ln 3$

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