

Show your work in all problems involving a calculation or derivation in order to receive credit. $R = 8.31451 \text{ J/K-mole} = 0.082058 \text{ L-atm/K-mole}$; $k_B = 1.38 \times 10^{-23} \text{ J/molecule}$; $1 \text{ L-atm} = 101.325 \text{ J}$. The exam counts 30% so the total number of points equals 300.

1) (85 points) A real gas can be described by the Virial Equation of State:

$$V = nRT/p + \alpha/(nRT) + \beta p/(nRT)^2$$

a) Calculate the work for the reversible, isothermal **expansion** of a real gas from pressure p_1 to pressure p_2 ($p_1 > p_2$). [Hint: If one makes a change of variable, $dV = (\partial V/\partial p)_{n,T} dp$.]

Take the hint; $(\partial V/\partial p)_{T,n} = -nRT/p^2 + 0 + \beta/(nRT)^2$

$$dw(\text{rev}) = -pdV = -p(\partial V/\partial p)_{T,n} dp = \{nRT/p + 0 - \beta p/(nRT)^2\} dp$$

Integrating with respect to p which is **not** constant, one obtains

$$w(\text{rev}) = nRT \ln(p_2/p_1) - \beta(p_2^2 - p_1^2)/(nRT)^2$$

b) Compare the work for a reversible isothermal expansion of a real gas with that for an irreversible isothermal expansion. Which is greater? Briefly explain. The initial and final pressures are the same in both cases.

One can show that $dw(\text{rev}) < dw(\text{irrev})$. The process is one of expansion so $dw < 0$. Therefore, the irreversible work is greater. (-4 is greater than -5). Many of you considered the magnitude. In this case, the inequality reverses, i.e. $|dw(\text{rev})| > |dw(\text{irrev})|$.

c) Derive expressions for $(\partial S/\partial p)_{n,T}$ and $(\partial G/\partial p)_{n,T}$ of a real gas. Each result should be a function solely of p , V , T , and n .

From the exactness of dG and $dG = -SdT + pdV$, the cross derivatives are equal and therefore $(\partial S/\partial p)_{T,n} = -(\partial V/\partial T)_{p,n} = -nR/p + \alpha/(nRT^2) + \beta p/(n^2 R^2 T^3)$. Divide $dG = -SdT + Vdp$ by dp and hold T constant, i.e. $dT = 0$. One obtains $(\partial G/\partial p)_{T,n} = V = nR/p + \alpha/(nRT) + \beta p/(nRT)^2$

2) (135 points) Monoclinic (M) and rhombic (R) sulfur are two crystalline forms of elemental sulfur. Under standard conditions, the two forms are in equilibrium at 368.54 K. The standard enthalpies of formation for monoclinic and rhombic sulfur at 298.15 K are 0.330 and 0.00 kJ/mole, respectively. The values of C_p° for monoclinic and rhombic sulfur are 25.9 and 22.6 J/K-mole, respectively.

a) Calculate the value of ΔS° at 298.15 K for the phase change $S(M) \rightarrow S(R)$.

Consider the sequence of the following reversible paths:

$S(M, 298.15 \text{ K}) \rightarrow S(M, 368.54 \text{ K}), \Delta S^\circ = C_p^\circ(M)\ln(368.54/298.15) = 5.49 \text{ J/K}$

$S(M, 368.54 \text{ K}) \rightarrow S(R, 368.54),$ (reversible since the phases are in equilibrium)

$\Delta S^\circ = \Delta H^\circ(368.54 \text{ K})/368.54 = -562 \text{ J}/(368.54 \text{ K}) = -1.53 \text{ J/K}$

$S(R, 368.54 \text{ K}) \rightarrow S(R, 298.15 \text{ K}), \Delta S^\circ = C_p^\circ(R)\ln(298.15/368.54) = -4.79 \text{ J/K}$

so for the net process, $\Delta S^\circ = (5.49) + (-1.53) + (-4.79) = -0.83 \text{ J/K}$

Note in the second step we require the standard enthalpy change at 368.54 K.

$\Delta H^\circ(M \rightarrow R, 298.15 \text{ K}) = 0 - 330 \text{ J} = -330 \text{ J}$.

$\Delta H^\circ(M \rightarrow R, 368.54 \text{ K}) =$

$$\begin{aligned} \Delta H^\circ(M \rightarrow R, 298.15 \text{ K}) + [C_p^\circ(R) - C_p^\circ(M)](368.54 - 298.15) \\ = -330 \text{ J} - 232 \text{ J} = -562 \text{ J}. \end{aligned}$$

b) You constructed a multi-step thermodynamic cycle in order to answer part (a). Pick one of the steps. Can you calculate the heat for this step? Briefly justify your answer.

Any of the steps considered above will suffice. Why? They are conducted under constant pressure conditions with only pressure-volume work so $dq = dH$. So for the first leg of the cycle, $q = C_p^\circ(M)\Delta T$. Reversibility is not required here.

c) Calculate the value of ΔG° for the phase change at 298.15 K and at 368.54 K.

The two phases are in equilibrium at 368.54 K so $\Delta G^\circ = 0$.

At 298.15 K, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -330 - (298.15)(-0.83) = -83 \text{ J}$

3) (80 points) The electronic ground state of O₂ is a triplet, i.e. the degeneracy $g = 3$. However, it also has a low lying singlet ($g = 1$) state. For the purposes of this problem, set the energy of the ground state to zero and the energy of the excited state to Δ .

a) Use the Boltzmann equation and calculate the average electronic energy of gaseous O₂ at an absolute temperature T.

$$\langle E \rangle = (N_1/N)(E_1) + (N_2/N)(E_2) / k_B T \text{ where } N_i/N = g_i \exp(-E_i) / q$$

$$q = 3 + \exp(-\Delta/k_B T), N_1/N = 3/q \text{ and } N_2/N = \exp(-\Delta/k_B T)$$

$$\langle E \rangle = [(3)(0) + (1)(\Delta)\exp(-\Delta/k_B T)] / [3 + \exp(-\Delta/k_B T)]$$

$$= \Delta \exp(-\Delta/k_B T) / [3 + \exp(-\Delta/k_B T)] = \Delta / [3 \exp(\Delta/k_B T) + 1]$$

Note the final algebraic step. It is not required here but greatly simplifies a later problem.

b) Suppose that the **total** molar energy for gaseous oxygen at a temperature T is E_0 . What is the molar enthalpy of the oxygen? What would happen to your answer if the oxygen were liquefied?

$H = E + pV$ but for an ideal gas, $pV = RT$ so $H = E_0 + RT$. However, when the oxygen is liquified, H and E are nearly identical so $H \approx E_0$.

c) Use the result from (a) to obtain the electronic contribution to the C_V .

$$C_V(\text{electronic}) = (d\langle E \rangle / dT) = d/dT \{ \Delta / [3 \exp(\Delta/k_B T) + 1] \}$$

$$= (-1) \{ \Delta / [3 \exp(\Delta/k_B T) + 1]^2 \} (d[3 \exp(\Delta/k_B T) + 1] / dT) \quad (\text{chain rule!})$$

$$= (\Delta^2 / k_B T^2) [3 \exp(\Delta/k_B T)] / [3 \exp(\Delta/k_B T) + 1]^2$$

d) Obtain an expression for the electronic contribution to the molar entropy at a high T and at low T. Is your result consistent with the Third Law of Thermodynamics? Discuss.

At high T, each of the 4 quantum mechanical states is equally probably (E/T goes to 0) so $W = 4$ and therefore $S = R \ln(4)$. At low T, only the 3 states with 0 energy are occupied so $W = 3$ and $S = R \ln(3)$. One expects $S = 0$ at 0 K but this result implies a non-degenerate ground state. This is not possible with non-interacting oxygen molecules. If the third law is correct, the oxygen molecules interact. Consider two bar magnets which pair up. One cancels the magnetism of the other and a non-degenerate state results.