

Problems: P5.11, P5.16, P5.24, P6.1, P6.4

HW6A Due Tuesday (02/19/08)

(There is no class Monday)

I have added a new problem (5.11) because you need to go through it anyway to do 5.16 properly, and the part b of it is quite novel. You have no expression yet derived for you for the temperature change due to a one step adiabatic expansion. Solving for the temperature change should be quite interesting and challenging. Remember, do not be in any rush to find the answer write down the connections you know that parallel the relations for the case of reversible adiabatic expansion. You will see some differences and that the final temperature can be determined, you have as many equations as unknown. I have also added another part to the extra question (EQ2). Here I want you to discover a subtle difference in how the integrals are done and how subscripts can contribute importantly to the meaning of the process.

EQ1) Consider isothermal expansion of one mole of nitrogen, treated as a van der Waals' gas. A) Compute the entropy due to the expansion if the gas expands from an initial molar volume that is 6 times the b parameter for the gas to a final molar volume that is 11 times the b parameter.

B) Compare this result with that of an ideal gas that expands over the same volumes.

EQ2) Consider the isothermal expansion of a van der Waals' gas from an initial volume and pressure of V_i and P_i to a final volume and pressure V_f and P_f , and we want the entropy for this change. Consider the following method to compute the entropy:

$$\Delta S = \int_{V_i}^{V_f} \left(\frac{\partial S}{\partial V} \right)_T dV + \int_{P_i}^{P_f} \left(\frac{\partial S}{\partial P} \right)_T dP$$

a) Explain whether this will give the correct entropy or not. If this is not a correct approach, explain what is wrong with this approach. If incorrect, suggest a correct method to compute the entropy.

b) Show for Ideal Gas that the two integrals $\int_{V_i}^{V_f} \left(\frac{\partial S}{\partial V} \right)_T dV$ and $\int_{P_i}^{P_f} \left(\frac{\partial S}{\partial P} \right)_T dP$ do give the same answer for this process.

c) Explain why these two integrals must give the same value for any gas with any equation of state, for this process.

d) Correct this form

$$a) \quad \Delta S = \int_{V_i}^{V_f} \left(\frac{\partial S}{\partial V} \right)_T dV + \int_{P_i}^{P_f} \left(\frac{\partial S}{\partial P} \right)_T dP$$

to be an accurate statement of the entropy change for this process, that DOES require 2 integrals. [If you are curious, you might prove to yourself you will get the same answer, at least for the I.G. as the other more direct method.]

EQ3) (This is a companion problem to P6.1) The combustion of methane generates $\Delta H_m^\circ = -890 \text{ kJ}$ per mole of methane. Compute the maximum non-expansion work that can be produced by the combustion of methane in an electrochemical fuel cell (at constant T and P).

Assume that the energy of a mole of methane is used to do work by a reversible heat engine that runs at 600K, and exhausts into the environment at 300K. Taking into account the theoretically maximal efficiency of this engine, compare the maximum work available from the heat engine with that available from the electrochemical fuel cell. Comment on which type of system can do more work.

P5.11) One mole of an ideal gas with $C_{V,m} = 5/2R$ undergoes the transformations described in the following list from an initial state described by $T = 250 \text{ K}$ and $P = 1.00 \text{ bar}$. Calculate q , w , ΔU , ΔH , and ΔS for each process.

- The gas undergoes a reversible adiabatic expansion until the final pressure is half its initial value.
- The gas undergoes an adiabatic expansion against a constant external pressure of 0.500 bar until the final pressure is half its initial value.
- The gas undergoes an expansion against a constant external pressure of zero bar until the final pressure is equal to half of its initial value.

P5.16) Calculate $\Delta S_{\text{surroundings}}$ and ΔS_{total} for the processes described in parts (a) and (b) of Problem P5.11 Which of the processes is a spontaneous process? The state of the surroundings for each part is as follows:

- 250 K, 0.500 bar
- 300 K, 0.500 bar

[The a and b in the answer at the back refer to the a and b of problem 5.11.]

P5.24) 1 mol of $\text{H}_2\text{O}(l)$ is supercooled to -2.25°C at 1 bar pressure. The freezing temperature of water at this pressure is 0.00°C . The transformation $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s)$ is suddenly observed to occur. By calculating ΔS , $\Delta S_{\text{surroundings}}$, and ΔS_{total} , verify that this transformation is spontaneous at -2.25°C . The heat capacities are given by $C_p(\text{H}_2\text{O}(l)) = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $C_p(\text{H}_2\text{O}(s)) = 37.7 \text{ J K}^{-1} \text{ mol}^{-1}$, and

$\Delta H_{fusion} = 6.008 \text{ kJ mol}^{-1}$ at 0.00°C . Assume that the surroundings are at -2.25°C . [*Hint:*

Consider the two pathways at 1 bar: (a) $\text{H}_2\text{O}(l, -2.25^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, -2.25^\circ\text{C})$ and (b) $\text{H}_2\text{O}(l, -2.25^\circ\text{C}) \rightarrow \text{H}_2\text{O}(l, 0.00^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, 0.00^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, -2.25^\circ\text{C})$. Because S is a state function, ΔS must be the same for both pathways.]