

## Thermodynamics. Problems. Sheet 4.

### Solutions of the problems.

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- 1) Determine the entropy of metallic Ag at 25°C, from the data on molar heat capacities given in the table. Consider that the heat capacity near 0 K approximately follows Debye's law.

T (K)	C <sub>p</sub> (J/mol K)
15	0.67
30	4.77
50	11.65
70	16.33
90	19.13
110	20.96
130	22.13
150	22.97
170	23.61
190	24.09
210	24.42
230	24.73
250	24.73
270	25.31
290	25.44
300	25.50

To solve this problem, we must consider 3 things:

- i) That  $s=0$  as  $T \rightarrow 0$  (Third Law).
- ii) That at  $T \rightarrow 0$ ,  $c_p \sim aT^3$  (Debye's approximation)
- iii) That at constant P,

$$\Delta s|_P = \int \frac{dq^{rev}|_P}{T} = \int \frac{dh|_P}{T} = \int_{T_i}^{T_f} \frac{c_p(T)dT}{T}$$

where lower case has been used for the molar variables  $s, q, h, c_p$  (entropy, heat, enthalpy, and heat capacity).

Then, we start by establishing  $c_p(T)$  at low  $T$ . To do so, we realize that the first point in the table must fulfil Debye's law. (In reality we should have two points satisfying it; then we could be sure they do.) We can then write:

$$c_p(T) = aT^3 \text{ (low } T) \Rightarrow 0.67 \frac{\text{J}}{\text{mol} \cdot \text{K}} = a15^3 \Rightarrow a = 1.985 \times 10^{-4} \frac{\text{J}}{\text{mol} \cdot \text{K}^4}$$

Then, and considering the Third Law ( $s=0$  as  $T \rightarrow 0$ ) we have:

$$\begin{aligned} s(T) &= \int_{0\text{K}}^{15\text{K}} dT' \frac{c_p(T')}{T'} + \int_{15\text{K}}^T dT' \frac{c_p(T')}{T'} = a \int_{0\text{K}}^{15\text{K}} dT' \frac{T'^3}{T'} + \int_{15\text{K}}^T dT' \frac{c_p(T')}{T'} \\ &= a \frac{1}{3} (15^3 - 0^3) + \int_{15\text{K}}^T dT' \frac{c_p(T')}{T'} = 0.223 \left( \frac{\text{J}}{\text{K}} \right) + \int_{15\text{K}}^T dT' \frac{c_p(T')}{T'} \end{aligned}$$

(Note, incidentally, that the first term is  $c_p(@15K)/3$ . In other words, the factor  $15^3$  does not enter into the computation of  $s$ . So, we need not compute this factor.)

To carry out the integral numerically, we use a computer spreadsheet (e.g., Excel) and apply the integration trapezoidal rule:

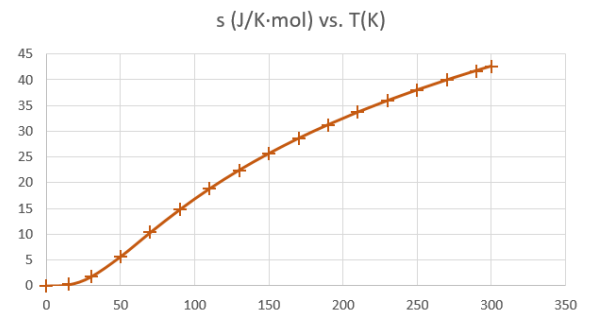
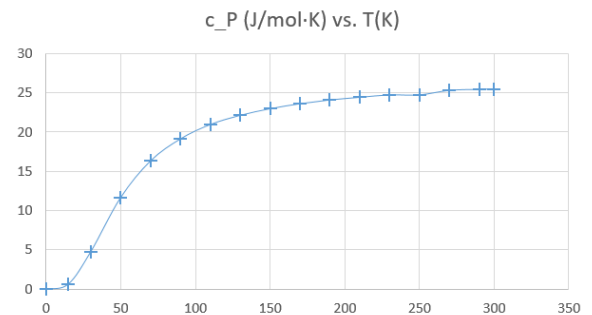
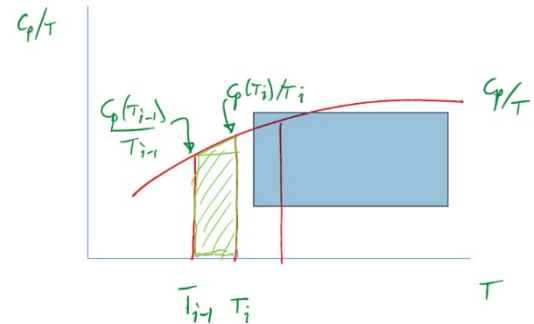
$$\int_a^b f(x)dx \approx (b-a) \cdot \frac{1}{2}(f(a) + f(b))$$

namely,

$$s_i = s_{i-1} + \frac{1}{2} \left[ \frac{c_p(T_i)}{T_i} + \frac{c_p(T_{i-1})}{T_{i-1}} \right] (T_i - T_{i-1})$$

We get the following result:

$T$ (K)	$c_p$ (J/mol K)	$c_p/T$	$s$ (J/K·mol)
0	0		0
15	0.67	0.0447	0.22
30	4.77	0.1590	1.75
50	11.65	0.2330	5.67
70	16.33	0.2333	10.33
90	19.13	0.2126	14.79
110	20.96	0.1905	18.82
130	22.13	0.1702	22.43
150	22.97	0.1531	25.66
170	23.61	0.1389	28.58
190	24.09	0.1268	31.24
210	24.42	0.1163	33.67
230	24.73	0.1075	35.91
250	24.73	0.0989	37.97
270	25.31	0.0937	39.90
290	25.44	0.0877	41.72
300	25.5	0.0850	42.58



To compute the entropy at 25 degrees C, we can give an approximate result, simply by saying:

$$s(298K) \approx s(300K) = 42 \frac{\text{J}}{\text{K}\cdot\text{mol}}$$

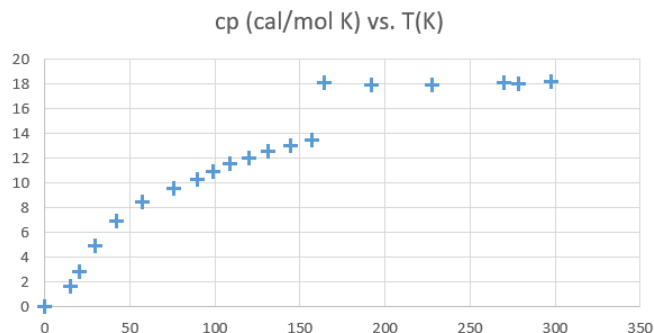
Or we can interpolate, e.g., linearly:

$$s(298K) \approx s(300K) - 0.085(300 - 298) = 42.41 \frac{\text{J}}{\text{K}\cdot\text{mol}}$$

- 2) Determine the molar entropy of CS<sub>2</sub> at 25°C from data on the molar heat capacities given in the table. The melting temperature is 161.11 K and the heat of melting is 1049.0 cal/mol. Near 0 K the system follows Debye's approximation.

T (K)	C <sub>p</sub> (cal/mol K)
15.05	1.65
20.15	2.87
29.76	4.96
42.22	6.97
57.52	8.50
75.54	9.57
89.37	10.31
99.00	10.98
108.93	11.59
119.91	12.07
131.54	12.58
144.31	13.05
156.83	13.53
163.93	18.10
192.30	17.91
227.34	17.93
269.69	18.08
278.22	18.06
297.43	18.17

This problem is similar to the previous one with the exception of the addition of the phase transition, through which the heat capacity suffers a discontinuity at constant temperature. Since we use molar quantities, we may either consider  $N=1$  mol or that we are dealing with molar quantities. We do the latter; thus, the lower case for extensive quantities ( $c_p, s, h_m, q^{rev}$ ).



The (molar) entropy will again be computed by integrating  $dq^{rev}/T$ . However, we should consider three stages of integration, plus one of extrapolation. The entropy at the desired temperature  $s(T)$  will equal the sum of the following terms:

- (1)  $s_s(T_m)$  = Sum of the entropy at the lowest temperature of 15.05 K, computed based on Debye's approximation for  $c_p$ , plus the integral of  $dq^{rev}/T$  for the solid phase, due to heating, from 15.05 K to the melting temperature ( $T_m = 161.11$  K);
- (2)  $\Delta s_m$  = Contribution from melting to the entropy;
- (3)  $s_l(297.43)$  = Integral of  $dq^{rev}/T$  for the liquid phase, due to heating, from  $T_m$  to the last data point in the table, for 297.43K.
- (4)  $T$  of 297.43 K is still below the desired temperature. Therefore, finally we will add a small increment as we linearly extrapolate  $s$  to the desired  $T$  (298 K).

### Development:

(1) First, we compute the entropy of the solid as a function of temperature up to the melting temperature,  $T_m$ :

$$s_s(T_m) = s(15.05) + \int_{15K}^{T_m} dT' \frac{c_p(T')}{T'}$$

where

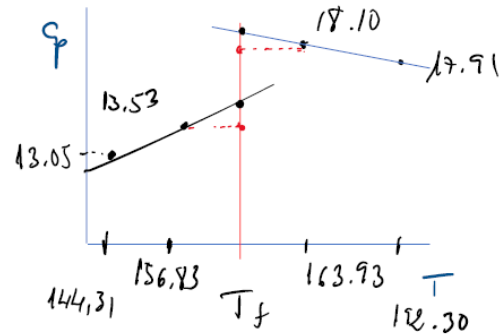
$$\begin{aligned} s(15.05) &= \int_{0K}^{15.05K} dT' \frac{c_p(T')}{T'} = a \int_{0K}^{15K} dT' \frac{T'^3}{T'} = a \frac{1}{3} ((15.05)^3 - 0^3) \\ &= \frac{c_p(15.05)}{3} = \frac{1.65}{3} \left[ \frac{\text{cal}}{\text{K} \cdot \text{mol}} \right] = 0.55 \left[ \frac{\text{cal}}{\text{K} \cdot \text{mol}} \right] \end{aligned}$$

where we've used that

$$a = \frac{c_p(15.05)}{15.05^3}.$$

The second term in the expression for  $s(T)$  should be carried out up to  $T_m$ . As before, we integrate using the trapezoidal rule. However, we do not have the value of  $c_p$  at the end of the integration temperature interval, that is, at 161.11 K ( $T_m$ ).

Therefore, we must figure it out. We could do that by linear extrapolation from the solid side (see figure). However, to simplify we assign the closest value (13.53). In stage 3, we will have a similar problem, and could extrapolate the  $c_p$  data from the liquid side (see figure), but we will use the closest value (18.10).



(2) For the melting stage, we compute the jump in entropy as:

$$\Delta s_m = \int \frac{dq^{rev}}{T_m} = \frac{h_m}{T_m} = \frac{1049.0}{161.11} = 6.51 \frac{\text{cal}}{\text{K} \cdot \text{mol}}$$

(3) The entropy up to 297.43 K equals (see table below):

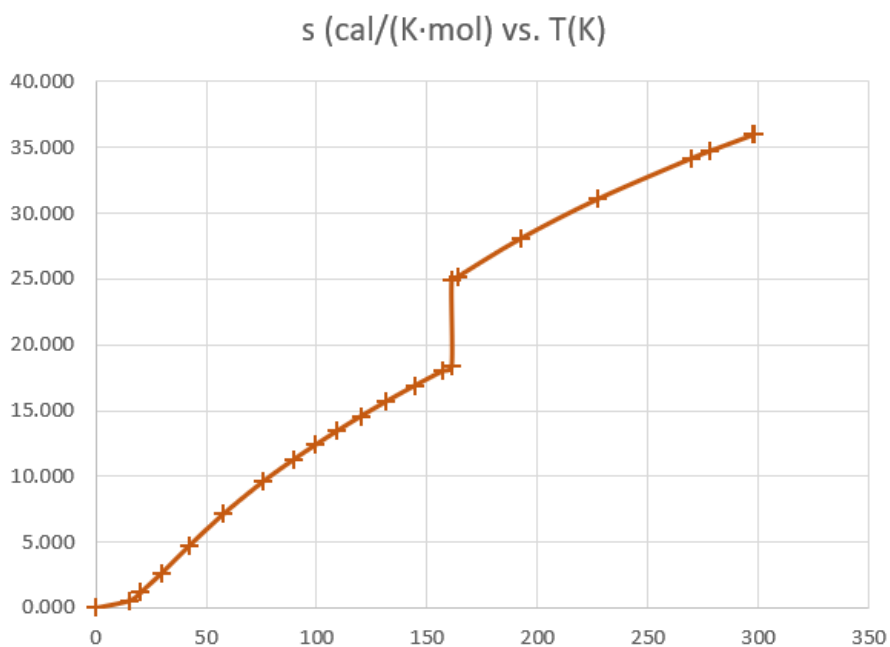
$$s(297.43) = s(15.05) + \int_{15K}^{T_m} \frac{c_p(T')}{T'} dT' + \frac{h_m}{T_m} + \int_{T_m}^{297.43} \frac{c_p(T')}{T'} dT' = 35.98 \frac{\text{cal}}{\text{K}}$$

(4) Finally, we extrapolate linearly from the last two points to the desired (nearby) temperature of 298 K:

$$\begin{aligned} s(298) &= s(297.43) + \frac{s(297.43) - s(278.22)}{297.43 - 278.22} (298 - 297.43) \\ &= 36.01 \frac{\text{cal}}{\text{K}} \end{aligned}$$

Note that the value at 297.43 is probably good enough an approximation.

T (K)	$c_p$ (cal/molK)	$c_p/T$	$s$ (cal/K·mol)	$\Delta s_m$
0	0		0.000	
15.05	1.65	0.110	0.550	
20.15	2.87	0.142	1.193	
29.76	4.96	0.167	2.678	
42.22	6.97	0.165	4.745	
57.52	8.5	0.148	7.138	
75.54	9.57	0.127	9.611	
89.37	10.31	0.115	11.285	
99	10.98	0.111	12.374	
108.93	11.59	0.106	13.453	
119.91	12.07	0.101	14.590	
131.54	12.58	0.096	15.732	
144.31	13.05	0.090	16.920	
156.83	13.53	0.086	18.026	
161.11	13.53	0.084	18.390	6.511
161.11	18.1	0.112	24.901	
163.93	18.1	0.110	25.215	
192.3	17.91	0.093	28.103	
227.34	17.93	0.079	31.116	
269.69	18.08	0.067	34.206	
278.22	18.06	0.065	34.768	
297.43	18.17	0.061	35.979	
298	18.18	0.061	36.015	



- 6) The heat of melting of ice at 0 °C and 1 atm is 79.1 cal/g ( $h_m$ ), while the heat of evaporation of water at the same pressure and 100 °C is 539 cal/g ( $h_v$ ). The mean heat capacity of water from 0 °C y 100 °C is 4.184 J/ K g ( $c_{pw}$ ). Compute the increase of entropy when 1 g ( $M$ ) of ice at 0 °C turns into vapor at 100 °C.

First, let us note that the heat capacity of water,  $c_{pw}$ , is equal to 1 cal/(K·g).

To compute the entropy increase we conceive of a reversible path from the initial state to the final state. Stages:

- 1) Ice melts at 0 °C.
- 2) Molten ice (water) heats up from 0 °C to 100 °C.
- 3) The water vaporizes at 100 °C.

The increase in entropy for the system is the sum of the entropy changes at each stage:  $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$

$$1) \Delta S_1 = \int \frac{dQ^{rev}}{T_m} = \frac{\Delta H_m}{T_m} = \frac{M \cdot h_m}{T_m} = 79.1 \times 1/273.15 = 0.2896 \text{ cal/K}$$

where subscript  $m$  stands for melting.

$$2) \Delta S_1 = \int \frac{dQ^{rev}}{T} = \int_{T_i}^{T_f} \frac{c_{pw} M dT}{T} = c_{pw} M \ln \frac{T_v}{T_m} = 1 \times 1 \times \ln \left( \frac{373.15}{273.15} \right) = 0.3120 \text{ cal/K}$$

$$3) \Delta S_1 = \int \frac{dQ^{rev}}{T_v} = \frac{\Delta H_v}{T_v} = \frac{M \cdot h_v}{T_v} = 539 \times 1/373.15 = 1.444 \text{ cal/K}$$

Finally, we have:

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = 2.046 \frac{\text{cal}}{\text{K}} = 8.56 \frac{\text{J}}{\text{K}}$$

- 7) Compute the variation of U, H, S and volume, as well as the final temperature in an adiabatic expansion of 1 dm<sup>3</sup> of O<sub>2</sub> at 5.00 atm and 25 °C to 1.00 atm of pressure. C<sub>p</sub> = 7.0 cal/ (K mol). Assume ideal gas behavior.

We need to assume a reversible process since we are not given enough information to solve the irreversible process. Now we need to identify all the necessary variables at the **initial (i) and the final (f) states** for the gas. What we know is:

$$V_i = 10^{-3} \text{ m}^3$$

$$P_i = 5 \text{ atm} = 5 \cdot 101325 \text{ Pa}$$

$$T_i = 273.15 + 25 = 298.15 \text{ K}$$

$$P_f = 1 \text{ atm} = 101325 \text{ Pa}$$

We will need  $\gamma \equiv c_p/c_v$ . We know  $c_p$ , and need  $c_v$ . According to Meyer's relation:  $c_v = c_p - R$ , where  $R=8.314 \text{ J/(K}\cdot\text{mol)}$ . Since  $c_p = 7.0 \text{ cal/ (K mol)} = 29.26 \text{ J/(K}\cdot\text{mol)}$ ,  $c_v = 20.95 \text{ J/(K}\cdot\text{mol)} = 5.0 \text{ J/(K}\cdot\text{mol)}$ . So,

$$\gamma = 1.3964 \text{ (nearly } 7/5, \text{ which would also be accepted).}$$

We don't know  $V_f$ , or  $T_f$  (needed to compute  $\Delta U$ ). Since the expansion is adiabatic, we can compute the final state using the adiabatic relations derived in class:

$$P_i V_i^\gamma = P_f V_f^\gamma \text{ gives us } V_f. \text{ And } V_i T_i^{\frac{1}{\gamma-1}} = V_f T_f^{\frac{1}{\gamma-1}} \text{ gives us } T_f; \text{ or we can get this from } T_f/T_i = (P_f/P_i)^{\frac{\gamma-1}{\gamma}}. \text{ Using these we get:}$$

$$V_f = 3.16 \times 10^{-3} \text{ m}^3$$

$$T_f = 188.8 \text{ K.}$$

We also need the number of moles, which can be obtained easily as  $N = \frac{P_i V_i}{RT_i} = 0.2044 \text{ moles}$ . Finally, we can compute the requested variables:

$$\text{Change in } V: \Delta V = (V_f - V_i) = 2.17 \times 10^{-3} \text{ m}^3$$

$$\text{Change in } U: \Delta U = N c_v \Delta T = N c_v (T_f - T_i) = -467 \text{ J}$$

$$\text{Change in } H: \Delta H = N c_p \Delta T = -655 \text{ J}$$

$$\text{Change in } S: \Delta S = \int \frac{dQ^{rev}}{T} = 0, \text{ since it is an adiabatic reversible process (therefore, isentropic).}$$

Note that for  $\Delta U$  we could have used  $\Delta U = Q + W$  with  $Q=0$  and

$$W = - \int_{V_i}^{V_f} dV P(V) = - \int_{V_i}^{V_f} dV P_i \left( \frac{V_i}{V} \right)^\gamma = \dots$$

and for  $H$  we could have used  $\Delta H = \Delta(U + PV)$ . But what we did is more direct.

- 8) 1.0 kg of ice at  $-10^{\circ}\text{C}$  is introduced in a thermally isolated recipient already containing 5.0 kg of water at  $30^{\circ}\text{C}$ . What is the variation of entropy in the process? The heat of melting of ice is  $79.67\text{ cal/g}$ , the heat capacity of ice is  $0.482\text{ cal/g K}$  and  $1.000\text{ cal/g K}$  the one of liquid water.

Let us list the inputs:

$$M_{ice} = 1\text{ Kg}$$

$$T_{ice,i} = -10^{\circ}\text{C} = 263.15\text{ K}$$

$$M_w = 5\text{ Kg}$$

$$T_{wi} = 30^{\circ}\text{C} = 303.15\text{ K}$$

$$c_{p,ice} = 0.482\text{ cal/(g}\cdot\text{K)}$$

$$c_{pw} = 1.000\text{ cal/(g}\cdot\text{K)}$$

$$h_m = 79.67\text{ cal/g}$$

We also need that ice melts at  $0^{\circ}\text{C}$ , i.e.,

$$T_m = 273.15\text{ K}.$$

The ice absorbs heat from the water, thereby reducing its temperature. Upon melting heat is absorbed and  $H$  is increased. Therefore, the ice melts and also raises its temperature. For the final state we assume that the ice and water are converted to a homogeneous body of water (no ice) at a final temperature,  $T_f$ . If this turns out not to be true, we should get some “crazy” result. If this is not the case, then our assumption should be correct.

To compute the entropy change we need to devise a reversible path that takes us from the initial state to the final state. For that, we will need the final temperature. So, first, let's determine  $T_f$ . We use the First Law to establish the final state:

$$\Delta H = \Delta(H_{ice} + H_w) = \int dQ^{rev}|_P = 0$$

as the system evolves without exchanging heat with the surroundings (only a little work). First, we write the equations for the enthalpy change due to the changes in the ice mass (all the way to the final temperature after melting). Ice heats up from  $-10^{\circ}\text{C}$  ( $T_{ice,i}$ ) to  $0^{\circ}\text{C}$  ( $T_m$ ), then it melts and then it (as molten ice, namely water) heats up from  $0^{\circ}\text{C}$  ( $T_m$ ) to the final temperature,  $T_f$ :

$$\Delta H_{ice} = \Delta H_{ice(-10,0)} + \Delta H_{melting} + \Delta H_{ice(0,T_f)}$$

where

$$\Delta H_{ice(-10,0)} = M_{ice} c_{p,ice} (T_m - T_{ice,i})$$

$$\Delta H_{melting} = M_{ice} h_m$$

$$\Delta H_{ice(0,T_f)} = M_{ice} c_{pw} (T_f - T_m)$$

Next, we write the change in the water enthalpy as it cools down from its initial temperature ( $T_{wi}$ ) to the final temperature ( $T_f$ ).

$$\Delta H_w = M_w c_{pw} (T_f - T_{wi})$$



By substituting these expressions into the statement for the First Law above ( $\Delta H = 0$ ), we obtain a linear equation in  $T_f$ . After solving for  $T_f$ , we obtain:

$$T_f = \frac{-c_{p,ice}M_{ice}(T_m - T_{ice,i}) - M_{ice}h_m + c_{pw}(M_{ice}T_m + M_wT_{wi})}{c_{pw}(M_{ice} + M_w)}$$

This is 284.06 K, or 10.9°C.

Now we compute the entropy change. We use a path with the following stages:

a) Heating of the ice from  $T_{ice,i}$  to  $T_m$ . The entropy change is:

$$\Delta S_a = \int \frac{dQ^{rev}}{T} = \int_{T_1}^{T_2} \frac{c_{p,ice}M_{ice}dT}{T} = c_{p,ice}M_{ice} \ln \frac{T_m}{T_{ice,i}}$$

b) Melting of the ice at constant temperature  $T_m$ :

$$\Delta S_b = \int \frac{dQ^{rev}}{T} = \frac{\Delta H_{melting}}{T_m} = \frac{M_{ice} h_m}{T_m}$$

c) Heating of the molten ice from  $T_m$  to  $T_f$  (like for a)):

$$\Delta S_c = \int \frac{dQ^{rev}}{T} = \dots = c_{pw}M_{ice} \ln \frac{T_f}{T_m}$$

d) Cooling of the water from  $T_{wi}$  to  $T_f$  (like for a)):

$$\Delta S_d = \int \frac{dQ^{rev}}{T} = \dots = c_{pw}M_w \ln \frac{T_f}{T_{wi}}$$

We get:

$$\Delta S_a = 75.2 \text{ J/K}$$

$$\Delta S_b = 1220.6 \text{ J/K}$$

$$\Delta S_c = 163.9 \text{ J/K}$$

$$\Delta S_d = -1360.3 \text{ J/K}$$

The sum of all these terms gives us:

$$\Delta S = 99.5 \text{ J/K} = 23.8 \text{ cal/K.}$$

It is important to note that the temperatures should not be rounded off to 1K precision. The reason is that the final entropy change is the difference between positive and negative contributions which are much larger in magnitude than their difference (compare 99.5 to 1360.3, for example). If the temperatures are rounded off to 1K precision, for example, the values of the entropy contributions will be off especially in stages c and d, giving a final result of 18.6 J/K or 4.4 cal/K.

- 9) a) The temperature of an ideal gas with constant heat capacity varies from  $T_1$  to  $T_2$ . Demonstrate that the variation of entropy of the gas is larger if this process takes place at constant pressure than at constant volume.
- b) The pressure of an ideal gas varies from  $P_1$  to  $P_2$  either through an isothermal transformation or through an isochoric transformation. Compute the variations of entropy in both cases and demonstrate that they have opposite sign.

First, note that the problem statement does not tell us whether the processes are reversible. However, we do not have further information. Therefore, we should assume the reversible case.

In this problem, we will make use of the expression given in class for a general process by an ideal gas, which we develop again here:

$$\begin{aligned}\Delta S &= \int \frac{dQ^{rev}}{T} = \int \frac{dU - dW^{rev}}{T} = \int \frac{dU + PdV}{T} = \int \frac{dU}{T} + \int \frac{PdV}{T} \\ &= \int_{T_1}^{T_2} \frac{C_V dT}{T} + \int_{V_1}^{V_2} \frac{NR dV}{V} = C_V \ln\left(\frac{T_2}{T_1}\right) + NR \ln\left(\frac{V_2}{V_1}\right)\end{aligned}$$

#### Part a)

First, note that the final state ( $f$ ) is different whether the carried process is carried at constant pressure or constant volume. This can be easily seen graphically.

Next, we develop the expressions for the change in entropy for each case:

Now, at constant pressure, the volume ratio is equal to the temperature ratio (Charles' law). Therefore,

$$\Delta S|_P = C_V \ln\left(\frac{T_2}{T_1}\right) + NR \ln\left(\frac{T_2}{T_1}\right) = (C_V + NR) \ln\left(\frac{T_2}{T_1}\right) = C_P \ln\left(\frac{T_2}{T_1}\right)$$

A much more direct way to arrive at the same result is as follows:

$$\Delta S|_P = \int \frac{dQ^{rev}|_P}{T} = \int \frac{dH|_P}{T} = \int \frac{C_P dT}{T} = C_P \ln\left(\frac{T_2}{T_1}\right)$$

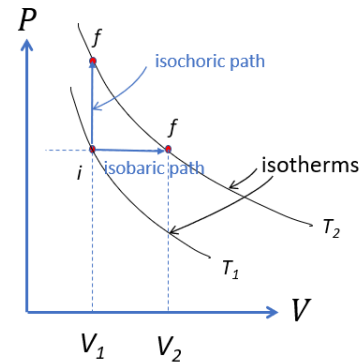
For the process at constant volume, the general expression for  $\Delta S$  leads to:

$$\Delta S|_V = C_V \ln\left(\frac{T_2}{T_1}\right)$$

Since  $C_p > C_v$  we have that

$$|\Delta S|_P > |\Delta S|_V$$

q.e.d. Note that the implication for the problem statement is that “larger” meant “larger in absolute value”.



## Part b)

Graphically, we have the situation shown in the figure at right. Again, the final state is different for each process. Again, we use the general expression for the change of entropy.

Again, for an **isochoric process** (constant volume), we have that

$$\Delta S|_V = C_V \ln \left( \frac{T_2}{T_1} \right)$$

On the other hand, for an **isothermal process** (constant temperature), we have that

$$\Delta S|_T = NR \ln \left( \frac{V_2}{V_1} \right)$$

To compare these two expressions, we must express them in terms of the initial and final pressures. We use:  $PV = NRT$ . For the isochoric process, we have that  $P \sim T$ , ergo,

$$\Delta S|_V = C_V \ln \left( \frac{P_2}{P_1} \right)$$

For the isothermal process, we have that  $P \sim V^{-1}$ , ergo,

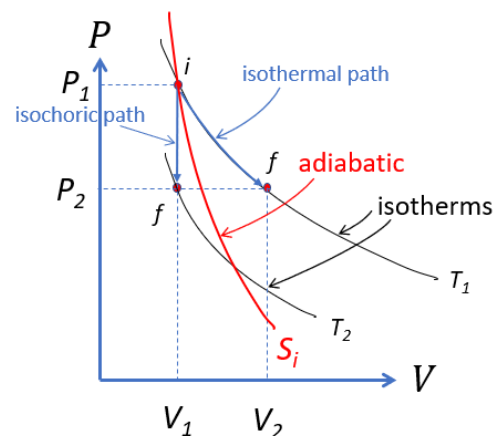
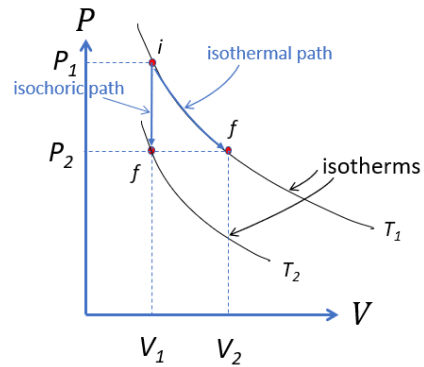
$$\Delta S|_T = NR \ln \left( \frac{P_1}{P_2} \right) = -NR \ln \left( \frac{P_2}{P_1} \right)$$

Since the sign of  $NR$  is the same as for  $C_V$ , we have that:

$$\text{Sign}(\Delta S|_V) = -\text{Sign}(\Delta S|_T)$$

Note that this is so, regardless of whether the initial pressure is larger or smaller than the final pressure. In other words, one process takes us to a lower entropy while the other process takes us to higher entropy.

This is very clear graphically when we consider the adiabatic to which the initial state ( $i$ ) belongs. Such adiabatic lines are isentropic lines; therefore, they are characterized by a particular value of the system's entropy. We can see clearly in the graph, the final-state point to the left of this adiabatic belongs to an adiabatic with a lower entropy value than the initial-point adiabatic, whereas the final-state point to the right belongs to an adiabatic with a higher entropy value. Note also that all the analysis and conclusions stand unchanged, had we chosen a lower  $T_1$  than  $T_2$ .



10) 2.00 mol of an ideal gas expand from an initial volume of 4.0 L to a final volume of 40.0 L at a constant temperature of 27 °C. Compute the variation of entropy of the system and the one of the surroundings in each of the following processes:

- a) Reversible expansion.
- b) Expansion against a constant pressure of 1 atm.
- c) Expansion against a vacuum.

The key to this problem is to see that, since the entropy is a state function, the difference in entropy between the initial and the final states is the same no matter what the path is. However, that of the environment changes.

Let us list the input variables:

$$N = 2 \text{ mol}$$

$$V_i = 4 \text{ liters}$$

$$V_f = 40.0 \text{ liters}$$

$$T = T_{env} = 27 \text{ °C} = 300.15 \text{ K} \approx 300 \text{ K}$$

$$P_{ext} = 1 \text{ atm} = 101325 \text{ Pa} \text{ (for part b)}$$

a) **Reversible isothermal process:**

For the ideal gas system we have (see class notes or problem 9b):

$$\Delta S_{sys} = \Delta S|_T = NR \ln\left(\frac{V_2}{V_1}\right) = 2 \text{ mol} \times 8.314 \left(\frac{\text{J}}{\text{mol}\cdot\text{K}}\right) \times \ln\left(\frac{40}{4}\right) = 38.3 \frac{\text{J}}{\text{K}}$$

For the ‘universe’ (meaning system plus environment), we have that  $\Delta S$  (equal to the total change:  $\Delta S_{env} + \Delta S_{sys}$ ) must be zero, therefore for the environment:

$$\Delta S_{env} = -\Delta S_{sys} = -38.3 \frac{\text{J}}{\text{K}}$$

Note that these results are independent of the temperature.

b) **Expansion against a constant pressure:**

The expansion is an irreversible process.

The  $\Delta S_{sys}$  is the same as for a), **38.3 J/K**.

The  $\Delta S_{env}$  must be computed. We realize that the process of heat transfer from the environment to the system  $Q_{env}(= -Q_{sys})$  is carried out at constant temperature for the environment. In this case, we can design a reversible path for the environment in such a way that

$$\Delta S_{env} = \int \frac{dQ_{env}^{rev}}{T_{env}} = \frac{\int dQ_{env}^{rev}}{T_{env}} = \frac{Q_{env}}{T_{env}} = \frac{-Q_{sys}}{T_{env}}$$

Now we can compute  $Q_{sys}$  by applying the First Law to the (irreversible) process we have,

$$Q_{sys} + W_{sys} = \Delta U = 0$$

since the system is an ideal gas (thus  $U = N\phi(T)$ ) and the initial and final states are at the same temperature:

$$\begin{aligned} Q_{sys} = -W_{sys} &= -\int_i^f -P_{ext}dV = P_{ext} \int_i^f dV = P_{ext}\Delta V \\ &= 101325 \times (40 - 4)10^{-3}\text{J} = 3.65 \text{ kJ} \end{aligned}$$

Ergo,

$$\Delta S_{env} \left( = \frac{-Q_{sys}}{T_{env}} \right) = \frac{-3650 \text{ J}}{300 \text{ K}} = -12.2 \frac{\text{J}}{\text{K}}$$

Additional comment: Note that the final pressure is 1.23 atm. Therefore, the gas can be expanded irreversibly against 1 atm (a lower pressure) to attain the desired final volume. As it does so the gas cools down, but it eventually captures all the heat necessary to bring its temperature up to the final temperature of 27 °C. If the pressure against which the gas expands happened to be greater than 1.23 atm, then it would not be able to arrive to the desired final volume (40 L).

### c) Expansion against a vacuum:

The expansion into a vacuum is also an irreversible process.

The  $\Delta S_{sys}$  is the same as for a), **38.3 J/K**.

To compute  $\Delta S_{env}$ , we can set  $P_{ext}$  equal to zero in the development for part b), to conclude that  $\Delta S_{env} = 0$ .

A more direct way is to say that the expansion into a vacuum implies no heat or work interactions with the environment, which stays unchanged through the gas expansion process. Therefore, the environment did not vary, and its entropy did not change.

- 14) A cylinder contains an internal piston at each side of which there are 1 mol of a monatomic ideal gas. The walls of the piston are rigid and diathermic and the system is submerged in a liquid bath of large capacity (a source of heat) at a 0 °C temperature. The initial volumes of the two gaseous subsystems are 10 liters and 1 liter, respectively. The piston is then displaced reversibly such that the final volumes are 6 liters and 5 liters, respectively. (i) Compute the work done by the system by means of the Helmholtz free energy change (rather than direct computation of the reversible work). (ii) Compute the heat exchanged with the liquid bath. (iii) Did both subsystems absorb heat?

This problem applies simple concepts given in class.

Because it is an isothermal reversible problem, we can compute the reversible work done on the system  $W$  as the change in its Helmholtz free energy. The work done by the system onto the surroundings will be minus this result, namely  $-\Delta F$ . (Recall that  $\Delta F = W = -W^{\text{useful}}$ .)

Let us list the input variables:

$$\begin{aligned} N_1 &= N_2 = 1 \text{ mol (constant)} \\ T_b &= 0^\circ\text{C} = 273.15 \text{ K} \\ V_{1i} &= 10 \text{ liters} \\ V_{1f} &= 6 \text{ liters} \\ V_{2i} &= 1 \text{ liter} \\ V_{2f} &= 5 \text{ liters} \end{aligned}$$

The Helmholtz free energy of a monatomic ideal gas is:

$$F(T, V, N) = U - TS$$

where  $U(T, V, N)$  is given by (see note at the end of the problem)

$$U = \frac{3}{2} NRT$$

and  $S(T, V, N)$  can be obtained from  $S(U, V, N)$  was derived in class, by substituting the above expression for  $U$ :

$$S = \frac{N}{N_0} S_0 + NR \ln \left[ \left( \frac{U}{U_0} \right)^{3/2} \frac{V}{V_0} \left( \frac{N}{N_0} \right)^{-5/2} \right]$$

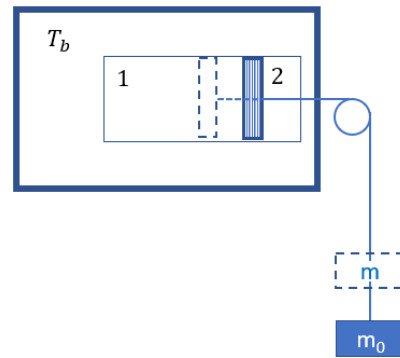
$$S = \frac{N}{N_0} S_0 + NR \ln \left[ \left( \frac{T}{T_0} \right)^{3/2} \frac{V}{V_0} \left( \frac{N}{N_0} \right)^{-1} \right]$$

where  $U_0 \equiv U(T_0, N_0) = \left( \frac{3}{2} \right) N_0 R T_0$ , and  $S_0 = \left( \frac{5}{2} \right) N_0 R - N_0 \left( \frac{\mu}{T} \right)_0$ .

Finally, the Helmholtz free energy for a monatomic ideal gas is:

$$F(T, V, N) = \frac{3}{2} NRT - \frac{N}{N_0} S_0 T - NRT \ln \left[ \left( \frac{T}{T_0} \right)^{3/2} \frac{V}{V_0} \left( \frac{N}{N_0} \right)^{-1} \right]$$

Note, incidentally, that it is easy to see that if we define  $F_0 = F(T_0, V_0, N_0)$ , then  $F_0 = U_0 - T_0 S_0$ .



Let us continue... Since we are only interested here in the changes in  $F$  for a process at constant  $T$  and  $N$ , we could have saved a lot of algebra by just considering the addends in  $U - TS$  that depend on  $V$ . For example, since the energy is only dependent on  $T$  and  $N$  (not dependent on  $V$ ), we could have ignored  $U$  from the start. In the end, the change in  $F$  of any one of the two subsystems is given by:

$$\Delta F = -NRT \ln \left( \frac{V_f}{V_i} \right)$$

Therefore, and finally, the change in the Helmholtz free energy for the composite system fulfills:

$$\Delta F = \Delta F_1 + \Delta F_2 = -N_1 RT_b \ln \left( \frac{V_{1f}}{V_{1i}} \right) - N_2 RT_b \ln \left( \frac{V_{2f}}{V_{2i}} \right)$$

(i) Computation of the work done by the system ( $-W$ ). Since  $N_1 = N_2$ ,

$$\Delta F = -N_1 RT_b \ln \frac{6 \cdot 5}{10 \cdot 1} = -N_1 RT_b \ln 3 = -2495 \text{ J} = W$$

**The work performed by the system is  $-W = +2495 \text{ J}$ .**

Note that the reversible work could have been obtained directly by integration of:

$$dW = -P(V)dV$$

for each of the subsystems, which is:

$$W = - \int P(V)dV = - \int_{V_i}^{V_f} \frac{NRT}{V} dV = -NRT \ln \left( \frac{V_f}{V_i} \right)$$

This leads to the same expression for  $\Delta F$  as the one given above. Note that, in general (for any system), although the isothermal work can be computed, if  $F(T, V, N)$  is available, it is equally easy (or easier) to compute the reversible work by using the change in  $F$ .

(ii) The heat exchanged by the (composite) system with the source can be computed by using the First Law:

$$Q = \Delta U - W$$

Since in this case (ideal gas)  $\Delta U = 0$ , we have that

$$Q = -W = 2495 \text{ J}$$

(iii) No. The subsystem that underwent the expansion (2) absorbed heat from the heat bath, whereas the subsystem that underwent the compression (1) released heat to the heat bath. The two amounts added together give  $Q$ , which is positive, indicating a net absorption of heat.

If we wanted to get the heats for each subsystem  $k$  ( $k = 1, 2$ ), we could compute it from the First Law as  $\Delta U_k = Q_k + W_k$  (where we use that  $\Delta U_k = 0$  since the temperature and number of mols stay constant, and the system is an ideal gas; otherwise, for another kind of system in general, having to compute it):

$$Q_k = -W_k = \Delta F_k \quad k = 1, 2$$

where (see above)

$$\Delta F_k = -N_k R T_b \ln \left( \frac{V_{kf}}{V_{ki}} \right)$$

With this, we get

$$Q_1 = -1160 \text{ J}$$

$$Q_2 = 3655 \text{ J}$$

where, indeed,  $Q_1 + Q_2 = Q$  is fulfilled.

Couple final notes:

- 1) In the class notes, we let the external mass be extinguished by the process (from  $m_0$  to 0), achieving final mechanical and thermal equilibrium in the subsystems. Here however, we don't, as the final pressures are not equal. This means that the final mass of the external weight is finite. Note we could have devised a problem in which the gas at higher initial pressure would get further compressed (and the gas at lower initial pressure would get expanded by increasing (rather than lowering) the external mass by adding (rather than subtracting) differentials of mass.
- 2) It is interesting to observe that the entire work performed by the system comes from the heat source. This is the result of the fact that the internal energy of the system did not change because both  $N$  and  $T$  remained constant and the internal energy of the ideal gas only depends on those. (In general, for an arbitrary system, this would not be true). Since here the internal energy does not change, all the heat transferred to the system is converted to reversible work. This would appear to violate the Second Law, which prohibits the complete conversion of heat into work, as the sole effect. The "as the sole effect" bit is crucial, because it requires that the system returns in a cycle to its initial state. In the current exercise, the entire heat is converted to work, but the system arrives to a different state from its initial state. Therefore, the Second Law is not violated. The entropy of the system has increased, whereas the entropy of the heat source has decreased by the same amount, as the total change in entropy for a reversible process for an isolated system is zero (in this case including the reversible work source, which does not contribute to the entropy).
- 3) Finally, we want to highlight that the energy equation is sometimes written as

$$U = \frac{N}{N_0} U_0 + \frac{3}{2} N R (T - T_0)$$

This would be identical to the energy function used earlier in the problem, provided that  $U_0$  is defined as:

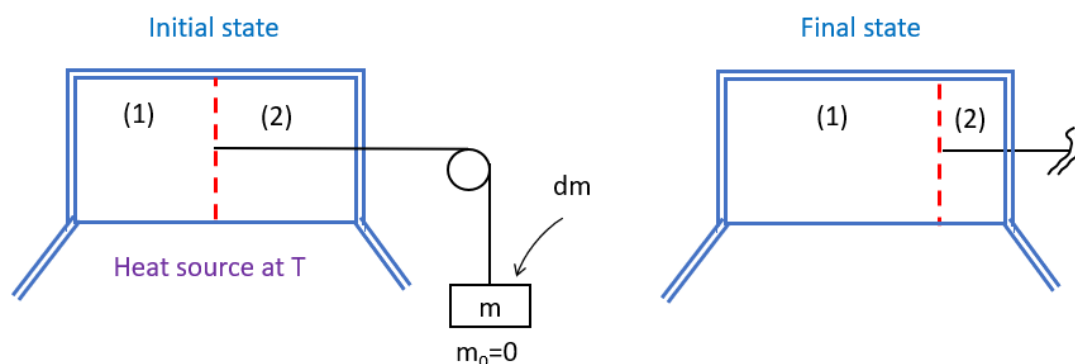
$$U(T_0, N_0) = \frac{3}{2} N_0 R T_0$$

(Showing this is left to the student.)



- 15) Two simple systems are within a cylinder, separated by a frictionless piston. Each subsystem is a mixture of  $\frac{1}{2}$  mol of  $N_2$  and  $\frac{1}{2}$  mol of  $H_2$  (which are considered to behave as ideal gases). Initially, the piston is at the center of the cylinder, having each subsystem a volume of 10 liters. The walls of the cylinder are diathermic. The system is in contact with a heat source at  $0^\circ C$ . The piston is permeable to  $H_2$ , but impermeable to  $N_2$ . Compute the work needed to displace the piston to a position where the subsystems' volumes are 5 and 15 liters.

In this problem an external implement (source of reversible work) is used to compress the non-permeating gas in one of the two compartments (and expand it in the other). It is interesting to point out the differences between a mixture of ideal gases (or ideal gas mixture) and a real mixture. In a real mixture, the interactions between the molecules account for some of its thermodynamic properties, so the fact that a gas is present in the system may change the properties of the other gas. However, here the two gases “do not see one another”, and behave as if they were independent. Let us see how.



Variable	Symbol	Initial value	Final value
Volume of subsystem 1	$V^{(1)}$	10 L	15 L
Volume of subsystem 2	$V^{(2)}$	10 L	5 L
Moles of nitrogen in sys.1	$N_A^{(1)}$	$\frac{1}{2}$ mol	$\frac{1}{2}$ mol
Moles of nitrogen in sys.2	$N_A^{(2)}$	$\frac{1}{2}$ mol	$\frac{1}{2}$ mol
Moles hydrogen in sys.1	$N_B^{(1)}$	$\frac{1}{2}$ mol	$\frac{3}{4}$ mol
Moles hydrogen in sys.2	$N_B^{(2)}$	$\frac{1}{2}$ mol	$\frac{1}{4}$ mol

We can easily see that there are two ways to solve this problem. One is to directly integrate the work expression. The other is by computing the difference in Helmholtz free energy  $F$ , which should equal (minus) to the reversible work done on the system ( $W$ ). Before we go on, we note that the work should be positive, since work is done on the system.  $F$  is a minimum at the initial state, and must therefore be higher in the final state. This is consistent with  ~~$\Delta F = -W$~~   $\Delta F = W > 0$ .

### First method: Computing the work directly.

For reversible work, we can write:

$$W = W^{(1)} + W^{(2)} = \int_i^f dW^{(1)} + \int_i^f dW^{(2)} = - \int_i^f P^{(1)} dV^{(1)} - \int_i^f P^{(2)} dV^{(2)}$$

Now we note that  $dV^{(1)} = -dV^{(2)}$ . Therefore, we can write

$$W = - \int_i^f (P^{(1)} - P^{(2)}) dV^{(1)}$$

Note that this expression is easily demonstrated if we equate  $W$  to the integral of the force on the piston times its displacement through the process, and relate the force to the pressures through a force balance on the piston. (This is left to the student.)

Now, for the ideal gas mixtures Boyle's equation is:

$$P = P_A + P_B = \frac{RT}{V} (N_A + N_B)$$

where subscript  $A$  refers to nitrogen, and  $B$  refers to hydrogen (for example). All variables refer to their values in either subsystem 1 or 2 (except  $T$  which is constant). Now, we note that for hydrogen,  $N_B$  changes, but such that its density remains constant, so  $N_B/V$  is constant through the process, and it is equal in both subsystems. Therefore, the hydrogen terms will cancel out. After some simple algebra, we get:

$$\begin{aligned} W &= - \int_i^f (P^{(1)} - P^{(2)}) dV^{(1)} = - \int_i^f (P_A^{(1)} - P_A^{(2)}) dV^{(1)} \\ &= - \int_i^f \left( \frac{N_A^{(1)} RT}{V^{(1)}} - \frac{N_A^{(2)} RT}{V^{(2)}} \right) dV^{(1)} \end{aligned}$$

Or, what is perhaps more straightforward to integrate:

$$W = - \int_{V_i^{(1)}}^{V_f^{(1)}} \frac{N_A^{(1)} RT}{V^{(1)}} dV^{(1)} - \int_{V_i^{(2)}}^{V_f^{(2)}} \frac{N_A^{(2)} RT}{V^{(2)}} dV^{(2)}$$

And this is simply

$$W = N_A^{(1)} RT \ln \left( \frac{V_i^{(1)}}{V_f^{(1)}} \right) + N_A^{(2)} RT \ln \left( \frac{V_i^{(2)}}{V_f^{(2)}} \right)$$

For the particular data of this problem  $N_A^{(1)} = N_A^{(2)} = N_A/2$ ; therefore,

$$W = \frac{1}{2} N_A RT \ln \left( \frac{V_i^{(1)}}{V_f^{(1)}} \frac{V_i^{(2)}}{V_f^{(2)}} \right) = \mathbf{327 \text{ joules}}$$

where we have substituted these input values:

$$N_A = 1 \text{ mol}$$

$$V_i^{(1)} = V_i^{(2)} = 10 \text{ liters}$$

$$V_f^{(1)} = 15 \text{ liters}$$

$$V_f^{(2)} = 5 \text{ liters}$$

Note that the work does not depend on the number of moles of hydrogen (or anything related to this gas).

**Second method:** Computing the work as ~~(minus)~~ the change in Helmholtz free energy:  ~~$W = -\Delta F$~~   $W = \Delta F$ .

Given that the work is easy to compute by the first methods, one wonders why we should use this more complex method. There's no reason if the equation of state is available. However, this exercise will help us understand some concepts.

To begin with, we need to see that  $F$  is the  $F$  for the total system and, due to its extensiveness, it is the sum of the  $F$ 's for each of the subsystems:

$$F = F^{(1)} + F^{(2)}$$

Also, for each subsystem (i) we have as natural variables:  $T, V^{(i)}, N_A^{(i)}, N_B^{(i)}$ . We omit the superscript for  $T$ , as  $T$  stays constant, but in general this may not be the case (although in that case, we may not be interested in using  $F$ ). So, we conclude that

$$\begin{aligned} F &= F(T, V^{(1)}, V^{(2)}, N_A^{(1)}, N_A^{(2)}, N_B^{(1)}, N_B^{(2)}) \\ &= F^{(1)}(T, V^{(1)}, N_A^{(1)}, N_B^{(1)}) + F^{(2)}(T, V^{(2)}, N_A^{(2)}, N_B^{(2)}) \end{aligned}$$

But not all these independent variables are independent from each other, since  $V^{(1)} + V^{(2)} = V$ , kept constant in this process, and similarly for the numbers of moles.

Now, to compute the  $\Delta F$  in the process, we need the expression for the  $F$  of a binary mixture of ideal gases, so we can use it in:

$$W = \Delta F = \Delta(F^{(1)} + F^{(2)}) = \Delta F^{(1)} + \Delta F^{(2)}$$

We have  $F$  for a single-component ideal gas (see problem 14):

$$F(T, V, N) = \frac{5}{2} NRT - \frac{N}{N_0} S_0 T - NRT \ln \left( \frac{T}{T_0} \right)^{5/2} - NRT \ln \left[ \frac{V}{V_0} \left( \frac{N}{N_0} \right)^{-1} \right]$$

obtained from its definition  $F = U - TS$ .  $S_0$  is  $S$  at some reference state characterized by  $N_0, V_0, T_0$ , and similarly for  $U_0 = U(T_0, N_0) = 5N_0RT_0/2$ , corresponding to a diatomic ideal gas at low temperature ( $c_v = 5R/2$ ).

We now need to somehow obtain  $F$  for a mixture of gases from the expression for a single-component gas. First, we should realize that, in general, when mixing two species together the energy, entropy, and thermodynamic potentials of the mixture will not simply be additive. The reason is that in general the two species could interact in non-obvious ways; therefore, the energetics of the interaction should be reflected somehow in these expressions, for example by means of interaction terms.

However, for the case of ideal gases, as we saw previously (Topics 1-3), the interaction is inexistent, as the gases behave as if the other gas was not present, and therefore we can assume that the energy, etc. are additive. More precisely, this is in fact true if these variables are expressed versus  $T, V$  (both shared by the different gases), and the components.<sup>1</sup> So, let us express the Helmholtz free energy for a mixture of two ideal gases  $A$  and  $B$  as:

<sup>1</sup> However, if we instead, used  $P$  (instead of  $T$ , for example), then, the pressure is not shared by the different species but "divided" among them, so to speak, and the

$$F = F_A + F_B$$

where  $F_j$  ( $j = A, B$ ) is as given above for a single component, but now written as

$$F_j(T, V, N_j) = \frac{5}{2} N_j RT - \frac{N_j}{N_0} S_{0j} T - N_j RT \ln \left( \frac{T}{T_0} \right)^{\frac{5}{2}} - N_j RT \ln \left[ \frac{V}{V_0} \left( \frac{N_j}{N_0} \right)^{-1} \right]$$

where for the reference state of each gas we have adopted the same  $N_0, V_0, T_0$ . We will be using this expression applied to each component in each subsystem.

Now, we are almost done:

$$\Delta F = \Delta(F^{(1)} + F^{(2)}) = \Delta(F_A^{(1)} + F_B^{(1)} + F_A^{(2)} + F_B^{(2)})$$

Recalling that index  $B$  is for hydrogen, for which “nothing changes”, it is easy to show in reference to the above expression for  $F_j(T, V, N_j)$  that its terms *added together* for the two subsystems ( $F_B^{(1)} + F_B^{(2)}$ ) remain constant in the process; in other words,

$$\Delta(F_B^{(1)} + F_B^{(2)}) = 0$$

This is because once they are added, they become the sum of addends which are proportional to  $N_B^{(1)} + N_B^{(2)}$ , (which is equal to the total moles of hydrogen, which is constant), times a function of the temperature and, in the case of the logarithm, a function of  $N_B^{(i)}/V^{(i)}$ , which, through the process, remains constant in both subsystems ( $i = 1, 2$ ).

Finally, focusing on the terms of the nitrogen gas ( $A$ ) in the expression for  $F_A^{(1)} + F_A^{(2)}$ , we see that the terms except the logarithmic ones depend only on  $T$  and the number of moles of  $A$ , which remain constant in the process. Therefore, these terms do not contribute to  $\Delta F$ . The only terms which contribute to  $\Delta F$  are the logarithmic terms. Considering that  $T, N_A^{(1)}$  and  $N_A^{(2)}$  are constant for the nitrogen, we have:

$$\begin{aligned} \Delta F &= \Delta(F_A^{(1)} + F_A^{(2)}) \\ &= -N_A^{(1)} RT \left( \ln \left( \frac{N_0}{V_0 N_A^{(1)}} V_f^{(1)} \right) - \ln \left( \frac{N_0}{V_0 N_A^{(1)}} V_i^{(1)} \right) \right) \\ &\quad - N_A^{(2)} RT \left( \ln \left( \frac{N_0}{V_0 N_A^{(2)}} V_f^{(2)} \right) - \ln \left( \frac{N_0}{V_0 N_A^{(2)}} V_i^{(2)} \right) \right) \\ &= \frac{N_A}{2} RT \ln \left( \frac{V_i^{(1)} V_i^{(2)}}{V_f^{(1)} V_f^{(2)}} \right) \end{aligned}$$

where we have used that  $N_A^{(1)} = N_A^{(2)} = N_A/2$ . This is the same expression as was obtained by computing the work directly.

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additivity cannot be guaranteed. To help see this, it is useful to think of the case of ideal gas mixtures, for which the different gases contribute to the pressure with their partial pressures, although they all have the same temperature.

16) Compute  $\Delta G$  and  $\Delta F$  for the vaporization of 1 mol of water at 1 atm and 100 °C. Density of water at those conditions is 0.958 g cm<sup>-3</sup>.

Key tip: Vaporization is a process that takes place at constant  $T$  and  $P$ .

Since this is a constant- $T, P$  process,  $\Delta G$  is zero (as  $dG = -SdT + VdP + \mu dN$ ).

For  $\Delta F$ , we must apply the definition of  $F$ . First, we note that  $F = F(T, V, N)$ . Therefore, since this is a process at constant  $T$  and  $N$ , all we need to do is figure out how  $F$  varies with  $V$ . To get  $F$  in the process we can easily integrate the differential Gibbs equation for  $F$  since:

$$dF = -SdT - PdV + \mu dN$$

The first two terms are zero, since  $dT = 0$  and  $dN = 0$ . And, since the pressure is constant the integral is trivial:

$$\Delta F = \int_i^f -PdV = -P\Delta V$$

where  $\Delta V = V_v - V_l$ , where subscripts  $v$  and  $l$  refer to the vapor and liquid phases.

So, we need to compute the change in volume. To a good approximation we only need the vapor volume, which is much larger than the liquid one. However, we can easily compute both.

To compute the vapor volume, we assume that water vapor at 1 atm and 100 °C behaves as an ideal gas:

$$V_v = \frac{NRT}{P}$$

The volume for the liquid water is:

$$V_l = \frac{N}{\rho_l} M = \frac{1}{0.958} 18 = 18.8 \text{ cm}^3/\text{mol}$$

where  $N$  is the number of mols (=1),  $\rho_l$  is the density of liquid water, and  $M$  is the molar mass of water, taken as 18 g cm<sup>-3</sup>.

Now putting it all together, we get:

$$\Delta F == -P(V_v - V_l) = -NRT + PV_l$$

So,

$$\begin{aligned} \Delta F &= -NRT + PV_l = \\ &= -1 \text{ mol} \cdot 8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}} \cdot 373.15 \text{ K} + 101325 \text{ Pa} \cdot 18.8 \text{ cm}^3 \cdot \frac{1 \text{ m}^3}{(100 \text{ cm})^3} \\ &= -3102 \text{ J} + 1.9 \text{ J} = -\mathbf{3.10 \times 10^3 \text{ J}} \end{aligned}$$

The contribution from the liquid water is negligible, as expected, since the vapor volume far exceeds the liquid volume.

17) Estimate  $\left(\frac{\partial U}{\partial V}\right)_T$  for nitrogen gas at 25°C and 1 atm assuming that it satisfies the van der Waals equation. (The constants for nitrogen are  $a=1.346 \times 10^6 \text{ cm}^6 \text{ atm mol}^{-2}$ , and  $b=38.52 \text{ cm}^3 \text{ mol}^{-1}$ ). *Hint:* Consider the Gibbs equation for the internal energy, and then find the appropriate Maxwell relation to transform the partial derivative of  $S$  to a manageable derivative for this problem.

We first note that the derivative in the problem statement is zero for an ideal gas. Therefore, it will not be zero for a van der Waals gas. The van der Waals equation is an equation of state which expresses the dependence between pressure  $P$ , temperature  $T$ , moles  $N$ , and volume,  $V$ , as

$$P = \frac{NRT}{V - bN} - a\left(\frac{N}{V}\right)^2$$

Therefore, we must connect the derivative for  $U$  in the problem statement to some derivative between these variables. To do so, we consider the Gibbs equation for the internal energy:

$$dU = TdS - PdV$$

to get:

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

We now need to transform the partial derivative of  $S$  to something that we can calculate using the van der Waals equation. To do so, we need to see that we need a thermodynamic potential for which  $S$  is a first derivative and  $V$  and  $T$  (and  $N$ ) are the natural variables. Such potential is the Helmholtz free energy,  $F$ , since

$$dF = -SdT - PdV$$

One of the Maxwell consistency relations is (after cancelling -1 on both sides):

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}$$

which we can trivially compute for the van der Waals gas, as:

$$-\left(\frac{\partial P}{\partial T}\right)_V = -\frac{NR}{V - bN}$$

Putting all together, we get:

$$\begin{aligned} \left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial S}{\partial V}\right)_T - P = T\left(\frac{\partial P}{\partial T}\right)_V - P = \\ &= T\frac{NR}{V - bN} - \left[\frac{NRT}{V - bN} - a\left(\frac{N}{V}\right)^2\right] = a\left(\frac{N}{V}\right)^2 \end{aligned}$$

Now, to compute this for  $N_2$  at 25°C and 1 atm, we need  $V/N$  at these conditions. Since at these conditions, nitrogen behaves similarly to an ideal gas, we can compute  $V/N$  approximately, as  $RT/P$ :

$$\frac{V}{N} \approx \frac{RT}{P} = \frac{8.314 \text{ J/(mol}\cdot\text{K)} * (273.15 + 25)\text{K}}{101325 \text{ Pa}} = 24.5 \times 10^{-3} \text{ m}^3/\text{mol}$$

If we use this approximation, note that parameter  $b$  (given in the statement) is, in fact, not needed. So, finally,

$$\left(\frac{\partial U}{\partial V}\right)_T = a \left(\frac{N}{V}\right)^2 = \frac{1.346 \times 10^6 \text{ cm}^6 \text{ atm mol}^{-2}}{(24.5 \times 10^3)^2 \text{ cm}^6 \text{ mol}^{-2}} = 2.24 \times 10^{-3} \text{ atm} = \mathbf{227 \text{ Pa}}$$

The smallness of this value (relative to 1 atm) indicates the smallness of the energy stored in the intermolecular forces for nitrogen at these conditions. Note that the units of pressure are the same as units of energy per unit volume.

Note: This is Levine's example 4.3.