

# The Curious Case of the Adiabatic, Irreversible Expansion

(ps. Benjamin Button dies at the end).

Calculate the final volume, temperature, work done by 0.5 mol of a gas ( $C_{v,m} = 12.47$  J/K/mol and  $C_{p,m} = 20.8$  J/K/mol) at 3 atm and 100 °C that irreversibly and adiabatically expands against an outside pressure of 1 atm.

b. What is the change in U and H?

## Answer:

Since  $P \cdot V = n \cdot R \cdot T$  for the initial *and final* states, we

have  $T_1 = \frac{P_1 V_1}{nR}$  (1) and  $T_2 = \frac{P_2 V_2}{nR}$  (2). Knowing

that  $n=0.5$  mol,  $T_1=373.15$  K,  $P_1 = 3$  atm = 303.975 kPa,  $P_2 = 1$  atm = 101.325 kPa we can calculate from (1) that  $V_1 = 5.103$  L. Now we need to know the volume and temperature of the final state ( $T_2$ ,  $V_2$ ) to calculate all the other thermodynamic variables; and while  $P \cdot V = n \cdot R \cdot T$  still works, we have a slight problem. This is because (2) has two unknown variables as adiabatic transitions have simultaneous changes in V and T. So, you cannot use (2) to do anything. Essentially, you have one equation with two unknown variables.

However, nature must provide a method to deal with this problem. First, since  $\partial U = \partial q + \partial w = \partial w$  in adiabatic transitions, which is always  $-P_{ext} \cdot \partial V$ . Also,  $\partial U = C_v \cdot \partial V$ . Thus, whether reversible or irreversible we know that:

$$n \cdot C_{v,m} \cdot \Delta T = -P_{ext} \cdot \Delta V \quad (3)$$

Where the irreversible and reversible differ is in how one takes care of the external pressure. In the reversible case, we set  $P_{ext}$  to  $n \cdot R / V$  and proceed as per the last handout. In our case, we do the following; first, redefine (3) as:

$n \cdot C_{v,m} \cdot (T_2 - T_1) = -P_{ext} \cdot (V_2 - V_1)$  Next, note that we can relate the final temperature to the final volume as:

$n \cdot C_{v,m} \cdot \left( \frac{P_2 V_2}{nR} - T_1 \right) = -P_{ext} \cdot (V_2 - V_1)$ . The amazing thing: we have all the variables in

this one equation defined except for  $V_2$ , which we can now calculate from:

$$0.5 \text{ mol} \cdot 12.47 \frac{\text{J}}{\text{K} \cdot \text{mol}} \cdot \left( \frac{101.325 \text{ kPa} \cdot V_2}{0.5 \text{ mol} \cdot 8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}}} - 373.15 \text{ K} \right) = -101.325 \text{ kPa} \cdot (V_2 - 5.103 \text{ L})$$



Prof. Preston T. Snee is a professor of physical chemistry and a well known Jackass.

Solving this for  $V_2$  gives a final volume of 11.226 L. Now we can calculate  $T_2$  two different ways: If we use (2), we get:  $T_2 = \frac{101.325kPa \cdot 11.226L}{0.5mol \cdot 8.314 J/K \cdot mol} = 273.6$  K. Or, we

could have used (3):  $n \cdot C_{v,m} \cdot \Delta T = -P_{ext} \cdot \Delta V$  which after we put in all the known variables is:  $0.5mol \cdot 12.47 J/K \cdot mol \cdot (T_2 - 373.15K) = -101.325kPa \cdot (11.226L - 5.103L)$  which makes  $T_2 = 273.6$  K!!! It's the same no matter how we calculate it!

The last thing I will do is calculate the work, which is  $n \cdot C_{v,m} \cdot \Delta T = 0.5mol \cdot 12.47 J/K \cdot mol \cdot (273.6K - 373.15K) = -621$  J. This is also the change in internal energy. The change in enthalpy is then:  $\Delta H = \Delta U + \Delta(P \cdot V) = \Delta U + n \cdot R \cdot \Delta T = -621$  J +  $0.5mol \cdot 8.314 J/K \cdot mol \cdot (273.6K - 373.15K) = -1.03$  kJ.

Let's see what we would get if the problem **was a reversible expansion** to a 1 atm final pressure. In this case, we use the adiabatic, reversible equation(s) of state:

Starting with  $\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{C_p}{C_v}}$  and plugging in numbers yields:

$\left(\frac{1atm}{3atm}\right) = \left(\frac{5.103L}{V_2}\right)^{\frac{0.5mol \cdot 20.8 J/K \cdot mol}{0.5mol \cdot 12.47 J/K \cdot mol}}$  After some manipulation we get:

$V_2 = \frac{5.103L}{\left(\frac{1atm}{3atm}\right)^{\frac{0.5mol \cdot 12.47 J/K \cdot mol}{0.5mol \cdot 20.8 J/K \cdot mol}}} = 9.86$  L. Now we can get the final temperature via

$\left(\frac{T_2}{T_1}\right)^{\frac{C_v}{nR}} = \left(\frac{V_1}{V_2}\right)$  which is  $\left(\frac{T_f}{373.15K}\right)^{\frac{0.5mol \cdot 12.47 J/K \cdot mol}{0.5mol \cdot 8.314 J/K \cdot mol}} = \left(\frac{5.103L}{9.86L}\right)$  which yields a  $T_2$  of

240.5 K. Likewise, the perfect gas law (2) gives  $T_2 = \frac{101.325kPa \cdot 9.86L}{0.5mol \cdot 8.314 J/K \cdot mol} = 240.3$  K,

I'm sure the very slight difference in the temperatures are due to truncation of significant figures when I did this on my calculator (they are obviously the same temperature).

Let's calculate the work to compare it to the irreversible result. Starting with  $\Delta w = n \cdot C_{v,m} \cdot \Delta T = 0.5mol \cdot 12.47 J/K \cdot mol \cdot (240.3K - 373.15K) = -828$  J.

Note that this is a greater negative quantity than the irreversible work (it was -621 J); this preserves the notion that we get the most work out (negative work) from a *reversible* system change. And how did that extra work come about? It's because the reversible expansion ends up with a much colder gas, which means more internal heat was converted to expansion work. Think of it like this: if the change in temperature is

$n \cdot C_{v,m} \cdot \Delta T = \partial w$  then  $\Delta T = \frac{\partial w}{n \cdot C_{v,m}}$ . Now since the reversible work is the most negative, then the reversible transition will cool the gas more compared to the irreversible transition.