



Statistical Molecular Thermodynamics



University of Minnesota

Homework Week 5

- Consider an ideal gas that occupies 3.00 dm^3 and has a pressure of 3.00 bar . This gas is compressed isothermally at a constant pressure of P_{ext} . Calculate the smallest value that P_{ext} can have if the final volume is 0.50 dm^3 . Using the value of P_{ext} obtained, calculate the work done on the gas.
 - 4500 J
 - 125 J
 - 300 J
 - 3225 J
 - 3000 J
 -

Answer:

If the gas is compressed isothermally, then we know from the ideal gas law that,

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{3.00 \text{ bar } 3.00 \text{ dm}^3}{0.500 \text{ dm}^3} = 18 \text{ bar}.$$

If P_{ext} is constant, then we also know,

$$w = - \int P_{ext} dV = -P_{ext} \Delta V = -18 \text{ bar} \times (0.500 - 3.00) \text{ dm}^3 = 45 \text{ dm}^3 \text{ bar}$$

Now we need to convert this to joules. The easiest way to do this is to remember that there are 10^5 pascals (Pa) per bar, and that one pascal is the equivalent of 1 newton per square meter, so

$$45 \text{ dm}^3 \text{ bar} \times 10^5 \frac{\text{Pa}}{\text{bar}} \times \frac{0.1^3 \text{ m}^3}{\text{dm}^3} = 4500 \frac{\text{Kg m}^2}{\text{s}^2} = 4500 \text{ J}$$

2. Calculate the work done when one mole of an ideal gas is compressed reversibly from 3.00 bar to 10.00 bar at a constant temperature of 300 K.

(a) 3002 kJ

(b) 2740 J

(c) 2494 kJ

(d) 3002 J

(e) 1.20 J

(f) 1.86 J

(g) 1.86 kJ

Answer:

We know from the ideal gas law that for one mole of gas,

$$V_1 = \frac{RT}{P_1} \text{ and } V_2 = \frac{RT}{P_2},$$

and thus $V_2/V_1 = P_1/P_2$, which we will use below. Moreover, as the compression is specified to be reversible, the external pressure must at every point be equal to (or, more accurately, only infinitesimally greater than) the internal pressure, which for an ideal gas is equal to nRT/V . Now it is simply a matter of making the appropriate substitutions into the following equations,

$$w = - \int P_{ext} dV = - \int \frac{nRT}{V} dV = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2} \quad (1)$$

$$= -1 \text{ mol} \times 8.315 \frac{\text{J}}{\text{mol K}} \times 300 \text{ K} \ln 0.3 = 3002 \text{ J} \quad (2)$$

3. Consider the reversible adiabatic expansion of one mole of an ideal gas from T_1 and P_1 to T_2 and P_2 . What is the correct relationship between the temperatures, pressures, and the molar constant pressure heat capacity, \bar{C}_P ?

(a) $\frac{T_1}{T_2} = R \ln \left(\frac{P_2}{P_1} \right)^{\bar{C}_P}$

(b) $\frac{T_1}{T_2} = R \ln \left(\frac{P_1}{P_2} \right)^{\bar{C}_P}$

(c) $\bar{C}_P \ln \left(\frac{T_1}{T_2} \right)^R = \frac{P_2}{P_1}$

(d) $\bar{C}_P \ln \left(\frac{T_1}{T_2} \right)^R = \frac{P_1}{P_2}$

(e) $\frac{T_1}{T_2} = \left(\frac{P_2}{P_1} \right)^{R/\bar{C}_P}$

(f) $\frac{T_1}{T_2} = \left(\frac{P_1}{P_2} \right)^{R/\bar{C}_P}$

(g) $\frac{T_1}{T_2} = R \left(\frac{P_2}{P_1} \right)^{\bar{C}_P}$

$$(h) \quad \frac{T_1}{T_2} = R \left(\frac{P_1}{P_2} \right)^{\bar{C}_P}$$

Answer:

Recall that $H = U + PV$. Therefore:

$$dH = dU + d(PV) = dU + PdV + VdP$$

There is no heat transfer in an adiabatic expansion, so $\delta q = 0$. Therefore, $dU = \delta w$. Also, recall that for an ideal gas, $\delta w = -PdV$. Using all of this information we can rewrite the differential dH :

$$\begin{aligned} dH &= dU + PdV + VdP \\ &= \delta w + PdV + VdP \\ &= -PdV + PdV + VdP \\ &= VdP \end{aligned}$$

For an ideal gas, $V = \frac{nRT}{P}$. Therefore:

$$dH = \frac{nRT}{P} dP$$

By definition, $C_P = \left(\frac{\partial H}{\partial T} \right)_P$. However, because the enthalpy of an ideal gas only depends on temperature, we can rewrite this as $dH = C_P dT$.

Equating the two expressions for dH gives the following:

$$C_P dT = \frac{nRT}{P} dP$$

Divide both sides by T and C_P :

$$\begin{aligned} \frac{dT}{T} &= \frac{nR}{C_P} \left(\frac{1}{P} \right) dP \\ &= \frac{R}{\bar{C}_P} \left(\frac{1}{P} \right) dP \end{aligned}$$

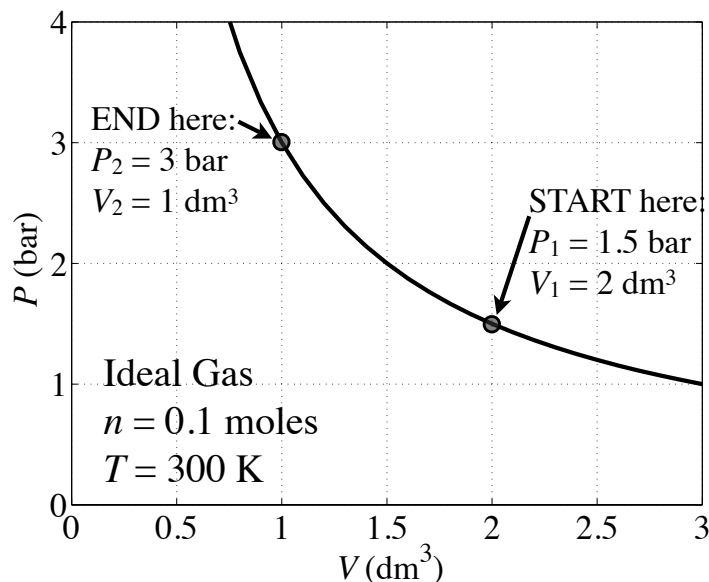
Integrate both sides of the above equation over their corresponding limits:

$$\begin{aligned} \int_{T_1}^{T_2} \frac{dT}{T} &= \int_{P_1}^{P_2} \frac{R}{\bar{C}_P} \left(\frac{1}{P} \right) dP \\ \ln \frac{T_2}{T_1} &= \frac{R}{\bar{C}_P} \ln \frac{P_2}{P_1} \\ &= \ln \left(\frac{P_2}{P_1} \right)^{R/\bar{C}_P} \end{aligned}$$

Taking the exponential of both sides delivers the desired result:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{R/\bar{C}_P}$$

4. Consider the isothermal compression of 0.1 moles of an ideal gas at 300 K from ($P_1 = 1.5 \text{ bar}$, $V_1 = 2 \text{ dm}^3$) to ($P_2 = 3 \text{ bar}$, $V_2 = 1 \text{ dm}^3$). The curve illustrates the internal pressure/volume relationship for the ideal gas at 300 K.



If the compression of the gas is carried out reversibly, which of the following statements is TRUE?

- (a) There will be no energy transferred as heat.
- (b) The change in the energy, U , will be positive.
- (c) The work required is the minimum for this compression.
- (d) The gas will cool (the temperature of the gas will go down).

Answer:

We know that it cannot be that there will be no energy transferred as heat. Why? Well, we know for an ideal gas the energy of the gas depends only on the temperature, so the total change in energy for this process must be zero since it is isothermal, i.e., $\Delta U = 0$. Because it is a reversible process, $w_{rev} = -q_{rev}$ and therefore,

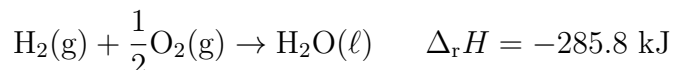
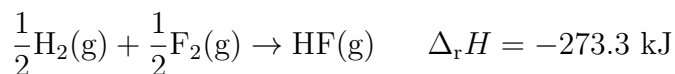
$$w_{rev} = -q_{rev} = -0.1RT \int_{V_1}^{V_2} \frac{dV}{V} = -0.1RT \ln \frac{V_2}{V_1}$$

So clearly, heat must transfer in an amount equal and opposite to the work done. In this case, the heat transferred is from the system to the surroundings, so the sign on q is negative (note that V_2 is smaller than V_1 , so the logarithm is a negative number).

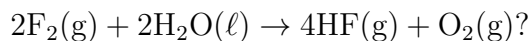
There is no increase in energy, as we just discussed, so so there is no positive energy increase. Also, the gas will not cool, even though *heat* leaves the system - it does so only to maintain a constant temperature (the compression is isothermal). If the temperature remains constant, it is not cooling.

We do know from lecture video 5.2 that the work done in the expansion and compression of a gas is dependent upon the path taken. For a reversible isothermal expansion of an ideal gas, the minimum work done is that done along the reversible path.

5. Given the following data,



What is the value of $\Delta_{\text{r}}H$ for the reaction,



(a) $\Delta_{\text{r}}H = -521.6 \text{ kJ}$

(b) $\Delta_{\text{r}}H = -11.7 \text{ kJ}$

(c) $\Delta_{\text{r}}H = -596.6 \text{ kJ}$

(d) $\Delta_{\text{r}}H = 1118.2 \text{ kJ}$

(e) $\Delta_{\text{r}}H = -1689.8 \text{ kJ}$

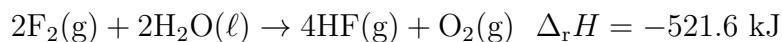
(f) $\Delta_{\text{r}}H = 559.1 \text{ kJ}$

Answer:

We can solve this using Hess's Law:

$$4 \times \left[\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{HF}(\text{g}) \right] \quad 4 \times \Delta_{\text{r}}H = -1093.2 \text{ kJ}$$

$$+ \quad 2 \times \left[\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \right] \quad 2 \times \Delta_{\text{r}}H = 571.2 \text{ kJ}$$



6. You have a gas that has a temperature dependent constant pressure heat capacity given by

$$\frac{\bar{C}_P(T)}{R} = 10 - 0.02 T \quad (50 > K > 300).$$

What is the change in the molar enthalpy of the gas if you raise the temperature from 100 K to 200 K? There are no phase transitions.

- (a) $\Delta \bar{H} = 0 R$
- (b) $\Delta \bar{H} = R$
- (c) $\Delta \bar{H} = 10 R$
- (d) $\Delta \bar{H} = 500 R$
- (e) $\boxed{\Delta \bar{H} = 700 R}$
- (f) $\Delta \bar{H} = 1000 R$

Answer:

$$\begin{aligned} H(T_2) - H(T_1) &= \int_{T_1}^{T_2} C_P dT \\ &= R \int_{100}^{200} (10 - 0.02T) dT \\ &= R(10T) \Big|_{100}^{200} - R \left(\frac{0.02}{2} T^2 \right) \Big|_{100}^{200} \\ &= R \left[10(200) - \frac{0.02}{2} (200)^2 - \left(10(100) - \frac{0.02}{2} (100)^2 \right) \right] \\ &= 700 R \end{aligned}$$

7. In lecture video 5.5, we learned that

$$\left(\frac{T_2}{T_1}\right)^{3/2} = \frac{V_1}{V_2}$$

for a monatomic ideal gas. Now consider a diatomic gas, N_2 , at 298 K. This gas is compressed reversibly and adiabatically from 15 dm^3 to 5.0 dm^3 . Assume that the heat capacity of this gas is $\bar{C}_V = 5R/2$, and that it behaves ideally. Calculate the final temperature, T_2 , of the gas.

- (a) 462 K
- (b) 751 K
- (c) 303 K
- (d) 1033 K
- (e) 433 K

Answer:

According to the definition, we know that

$$dU = n\bar{C}_V dT = \frac{5}{2}nRdT$$

Assuming ideal behavior, and noting the reversible nature of the compression, we can use:

$$\delta w = -PdV = -\frac{nRT}{V}dV$$

The problem tells us that the gas is compressed adiabatically; therefore, $\delta q = 0$ and $dU = \delta w$.

Setting the two above equations equal to one another allows us to obtain an expression that we can use to find the final temperature.

$$\begin{aligned} dU &= \delta w \\ \frac{5}{2}nRdT &= -\frac{nRT}{V}dV \\ \frac{5}{2}\frac{dT}{T} &= -\frac{dV}{V} \end{aligned}$$

Integrating both sides of the equation gives the following:

$$\frac{5}{2} \ln \frac{T_2}{T_1} = -\ln \frac{V_2}{V_1}$$

Inserting the information given in the problem allows us to solve for T_2 :

$$\begin{aligned} \ln \left(\frac{T_2}{298 \text{ K}} \right) &= -\frac{2}{5} \ln \left(\frac{5.00 \text{ dm}^3}{15.0 \text{ dm}^3} \right) \\ \left(\frac{T_2}{298 \text{ K}} \right) &= e^{0.4394} \end{aligned}$$

$$\boxed{T_2 = 462 \text{ K}}$$

8. Consider a 20.0 g sample of copper at 350 K placed into 100.0 g of water at 293 K. Heat is quickly transferred from the copper to the water, and the metal and water soon reach the same temperature (the zeroth Law!) What is the final temperature of the water? The molar heat capacities of copper and water are $24.5 \text{ J} \cdot \text{K}^{-1}$ and $75.3 \text{ J} \cdot \text{K}^{-1}$, respectively. The atomic weight of copper is 63.546 g/mol and the molecular weight of water is 18.015 g/mol.

- (a) 294.0 K
- (b) 304.9 K
- (c) 266.3 K
- (d) 303.5 K
- (e) 310.2 K

The energy of the system must be conserved, so any heat lost by the copper is gained by the water.

$$\Delta H = q = n\overline{C}_p\Delta T$$

Let x be the final temperature of the system. The heat lost by the copper is:

$$-q_{\text{Cu}} = -\left(\frac{20.0 \text{ g}}{63.546 \text{ g} \cdot \text{mol}^{-1}}\right) (24.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(x - 350 \text{ K})$$

Similarly, the heat gained by the water is:

$$q_{\text{water}} = \left(\frac{100.0 \text{ g}}{18.015 \text{ g} \cdot \text{mol}^{-1}}\right) (75.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(x - 293 \text{ K})$$

Set these two equations equal to one another to solve for the final temperature, x , of the system:

$$\begin{aligned} -q_{\text{Cu}} &= q_{\text{water}} \\ -(7.7109 \text{ J} \cdot \text{K}^{-1})x + 2698.8 \text{ J} &= (418.0 \text{ J} \cdot \text{K}^{-1})x - 1.225 \times 10^5 \text{ J} \end{aligned}$$

$$1.25168 \times 10^5 \text{ K} = 425.7x$$

$$\boxed{x = 294.0 \text{ K}}$$

Does it surprise you that dropping a piece of copper 57 K warmer than a bath of water having a mass only 5 times larger than that of the copper warms the water by only 1 K? The reason is the lower molecular weight of water (so more moles per mass), the higher heat capacity of water (so more places to store heat), and the greater mass of the water.

9. Calculate the work done in the isothermal reversible expansion of one mole of CH₄ (g) from 1.00 dm³ to 10.00 dm³ at 300 K. Treat methane as a van der Waals gas. The van der Waals gas constants for methane are: $a = 2.3026 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2}$ and $b = 0.043067 \text{ dm}^3 \cdot \text{mol}^{-1}$.

- (a) -4100 J
- (b) 5630 J
- (c) -5.63 kJ
- (d) -46.37 J
- (e) -230.07 J
- (f) -2.307 kJ

Answer:

We know from lecture video 2.2 that the van der Waals equation of state is

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

and for a reversible expansion we may use the equation of state to know the external/internal pressure at each point,

$$\begin{aligned} w &= - \int P d\bar{V} = - \int_{\bar{V}_1}^{\bar{V}_2} \left(\frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \right) d\bar{V} \\ &= -RT \ln \frac{\bar{V}_2 - b}{\bar{V}_1 - b} + \frac{a(\bar{V}_2 - \bar{V}_1)}{\bar{V}_2 \bar{V}_1} \\ &= -0.08314 \frac{\text{dm}^3 \cdot \text{bar}}{\text{mol} \cdot \text{K}} \cdot 300\text{K} \cdot \ln \frac{10 \text{ dm}^3 \cdot \text{mol}^{-1} - 0.043067 \text{ dm}^3 \cdot \text{mol}^{-1}}{1 \text{ dm}^3 \cdot \text{mol}^{-1} - 0.043067 \text{ dm}^3 \cdot \text{mol}^{-1}} \\ &\quad + \frac{2.3026 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2} (10 \text{ dm}^3 \cdot \text{mol}^{-1} - 1 \text{ dm}^3 \cdot \text{mol}^{-1})}{10 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot 1 \text{ dm}^3 \cdot \text{mol}^{-1}} \\ &= -56.35 \frac{\text{dm}^3 \cdot \text{bar}}{\text{mol}} = -5.63 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

10. Given the following data for water, determine $\Delta_{\text{vap}}H^\circ$ at 298 K and constant pressure:

$$\Delta_{\text{vap}}H^\circ \text{ at } 373 \text{ K} = 40.7 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\bar{C}_P(l) = 75.2 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$$

$$\bar{C}_P(g) = 33.6 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$$

(a) $43.8 \text{ J} \cdot \text{mol}^{-1}$

(b) $149.3 \text{ J} \cdot \text{mol}^{-1}$

(c) $149.3 \text{ kJ} \cdot \text{mol}^{-1}$

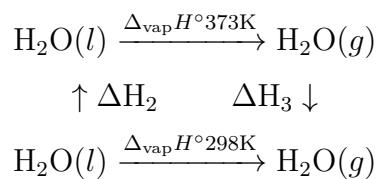
(d) $48.9 \text{ J} \cdot \text{mol}^{-1}$

(e) $40.7 \text{ kJ} \cdot \text{mol}^{-1}$

(f) $48.9 \text{ kJ} \cdot \text{mol}^{-1}$

(g) $43.8 \text{ kJ} \cdot \text{mol}^{-1}$

Answer:



$$\begin{aligned} \Delta_{\text{vap}}H^\circ(298)\text{K} &= \Delta H_2 + \Delta H_3 + \Delta_{\text{vap}}H^\circ(373)\text{K} \\ &= (75 \text{ K}) \times (75.2 \text{ J} \cdot \text{mol}^{-1}\text{K}^{-1}) + (-75 \text{ K}) \times (33.6 \text{ J} \cdot \text{mol}^{-1}\text{K}^{-1}) + 40.7 \text{ kJ} \cdot \text{mol}^{-1} \\ &= 43.8 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$