

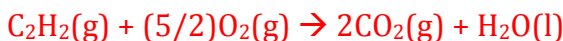
Thermodynamics Unit - RAQ

Consider the following CHEMICAL CHANGE:

Acetylene (C_2H_2) combusts in oxygen to form carbon dioxide and water.

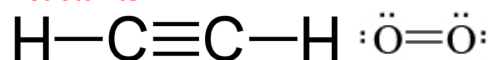
1. Estimate the enthalpy of combustion of acetylene using bond energies data.

First write the balanced equation where the coefficient of acetylene is 1:



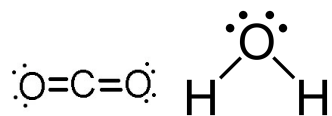
Then, draw the structures for each species:

Reactants:



Two C-H bonds, one $C \equiv C$ bond and one O=O bond

Products:



Two C=O bonds and two O-H bond.

$$\Delta H = \sum nBE_{react} - \sum nBE_{prod}$$

$$\Delta H = [1(2 \times 413) + 1(1 \times 835) + \frac{5}{2}(1 \times 498)] - [2(2 \times 799) + 1(2 \times 463)]$$

$$\Delta H = -1216 \frac{kJ}{mol}$$

All combustion reactions are exothermic and so have negative ΔH values.

A more thorough understanding can be gained by thinking through how energy is absorbed and released through the breaking and formation of chemical bonds:

Breaking Bonds = Requires Energy

Forming Bonds = Releases Energy

All tabular values for bond energies are positive, but you can imagine that for the bonds that are breaking (reactants), energy is put into the system and for bonds that are forming (products), energy is released out of the system. So:

$$\Delta H = +[\text{Bond Energy of Reactants}] + -[\text{Bond Energy of Products}]$$

Single Bond Energies (kJ/mol of bonds)

	H	C	N	O	S	F	Cl
H	436						
C	413	346					
N	391	305	163				
O	463	358	201	146			
S	347	272	—	—	226		
F	565	485	283	190	284	155	
Cl	432	339	192	218	255	253	242

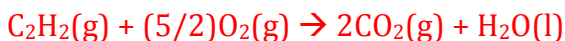
Multiple Bond Energies (kJ/mol of bonds)

C=C	602	C=N	615	C=O	799
C≡C	835	C≡N	887	C≡O	1072
N=N	418	O=O	498	N≡N	945

2. Calculate the enthalpy of combustion of one mole of C_2H_2 using heats of formation data found on the course website using your personal wireless device.

(Values found on course website)

First write the balanced equation were the coefficient of acetylene is 1:



$$\Delta H = \sum n\Delta_f H^\circ_{prod} - \sum n\Delta_f H^\circ_{react}$$

$$\Delta H = [(2\Delta_f H^\circ_{CO_2(g)}) + (1\Delta_f H^\circ_{H_2O(l)})] - [(1\Delta_f H^\circ_{C_2H_2(g)}) + (\frac{5}{2}\Delta_f H^\circ_{O_2(g)})]$$

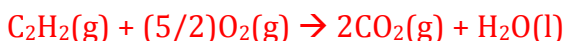
$$\Delta H = [2(-393.5) + 1(-286)] - [1(227) + \frac{5}{2}(0)]$$

$$\Delta H = -1300 \frac{kJ}{molrxn} (\frac{1molrxn}{1molC_2H_2}) = -1300 \frac{kJ}{molC_2H_2}$$

3. Calculate the change in entropy for this reaction using standard molar entropy data found on the course website.

(Values found on course website)

First write the balanced equation were the coefficient of acetylene is 1:



$$\Delta S^\circ_{rxn} = \sum nS^\circ_{prod} - \sum nS^\circ_{react}$$

$$\Delta S^\circ_{rxn} = [(2S^\circ_{CO_2(g)}) + (1S^\circ_{H_2O(l)})] - [(1S^\circ_{C_2H_2(g)}) + (\frac{5}{2}S^\circ_{O_2(g)})]$$

$$\Delta S^\circ_{rxn} = [2(214) + 1(70)] - [1(201) + \frac{5}{2}(205)]$$

$$\Delta S^\circ_{rxn} = -215.5 \frac{J}{K * molrxn}$$

4. Calculate the change in Gibbs free energy for this reaction. Is there ever a temperature where this reaction would be non-spontaneous? If so, what is that temperature? If not, why?

Work:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = -1300000 \frac{J}{mol} - (298K)(-215.5 \frac{J}{mol})$$

$$\Delta G^\circ = -1235781 \frac{J}{mol} \approx -1236 \frac{kJ}{mol}$$

Temp where non - spont :

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

$$\Delta H^\circ = T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-1300000 \frac{J}{mol}}{-215.5 \frac{J}{mol}} = 6032 \text{ K}$$

5. Imagine this reaction was run at constant pressure and temperature, what is the work for this process (combustion of 4 g C₂H₂)?



$$w = -P_{\text{ext}}\Delta V = -\Delta n_{\text{gas}}RT$$

$$w = -(2 \text{ mol}_{\text{prod}} - \frac{7}{2} \text{ mol}_{\text{react}})(8.314 \frac{J}{\text{molK}})(298K)$$

$$w = 3716 \frac{J}{\text{molrxn}}$$

For 4g :

$$w_{4g} = 3716 \frac{J}{\text{molrxn}} \left(\frac{1 \text{ molrxn}}{1 \text{ molC}_2\text{H}_2} \right) \left(\frac{1 \text{ molC}_2\text{H}_2}{26 \text{ gC}_2\text{H}_2} \right) (4 \text{ gC}_2\text{H}_2)$$

$$w_{4g} = 571.7J$$

Positive work indicates that work was done ON the system. The moles of gas in the reaction chamber decreased as the reaction progressed forward, meaning the gas was compressed by the external pressure – work done ON the system.

6. At constant pressure, use the change in enthalpy and the work to find the change in internal energy for this process (combustion of 4 g C₂H₂)?

$$\Delta U = q + w$$

At constant pressure $\Delta H = q_p$

$$\Delta U = \Delta H + w$$

$$\Delta H_{4g} = \Delta H^\circ_{rxn} n_{C_2H_2}$$

$$\Delta H_{4g} = -1300 \frac{kJ}{mol_{rxn}} \left(\frac{1 mol_{rxn}}{1 mol_{C_2H_2}} \right) \left(\frac{1 mol_{C_2H_2}}{26 g_{C_2H_2}} \right) (4 g_{C_2H_2})$$

$$\Delta H_{4g} = -200 kJ$$

$$\Delta U = q + w$$

$$\Delta U_{4g} = -200,000 J + 571.7 J = -199.4 kJ$$

7. 4 g of acetylene was combusted in a bomb calorimeter that had a heat capacity of 3.51 kJ/C for the device and contained 2000 g of water ($C = 4.184 \text{ J/g C}$) to absorb the heat as well. What is the expected temperature change in such a calorimeter given the complete combustion of the 4 g of the fuel.

In a bomb calorimeter the heat measured is equal to the change in internal energy.

$$\Delta U = q + w = -200 kJ + 0.572 kJ = -199.4 kJ$$

This is the internal energy change for this combustion reaction in general. In a bomb calorimeter, there would be no expansion or compression work. So the internal energy change would all be experienced by a heat exchange between the system and the calorimeter/water surroundings.

$$\Delta U = q_{sys} = -q_{surroundings} = -(q_{cal} + q_{water})$$

$$\Delta U = -(C_{cal}\Delta T + m_{water}C_{water}\Delta T)$$

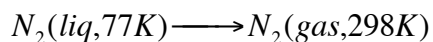
$$\Delta U = -\Delta T(C_{cal} + m_{water}C_{water})$$

$$-199.4 kJ = -\Delta T[3.51 kJ^\circ C^{-1} + (2000 g)(0.004184 kJ g^{-1} C^{-1})]$$

$$\Delta T = -199.4 kJ \div -11.88 kJ^\circ C^{-1}$$

$$\Delta T = 16.8^\circ C$$

Consider the following PHYSICAL CHANGE:



and the following THERMODYNAMIC DATA for N_2 :

$$\Delta H^\circ_{vaporization} = 5.56 \text{ kJ mol}^{-1}$$

$$C(N_{2gas}) = 29.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T_b = 77 \text{ K}$$

$$T_{surr} = 298 \text{ K}$$

1. How much heat is absorbed during this change given 4 moles of N₂?

Work:

$$q = n\Delta H_{\text{vap}}^{\circ} + nC_{\text{gas}}\Delta T$$

$$q = (4\text{mol})(5.56 \frac{\text{kJ}}{\text{mol}}) + (4\text{mol})(0.0291 \frac{\text{kJ}}{\text{mol}})(298\text{K} - 77\text{K})$$

$$q = 47.9644 \text{ kJ}$$

2. What is the work for this process (assuming the initial volume of the liquid is zero?)

$$w = -\Delta n_{\text{gas}}RT = -(4\text{mol} - 0\text{mol})(8.314\text{Jmol}^{-1}\text{K}^{-1})(298\text{K}) = -9910.29 \text{ J} = -9.91 \text{ kJ}$$

3. What is the change in internal energy for this process?

$$\Delta U = q + w = 47.96 \text{ kJ} - 9.91 \text{ kJ} = +38.05 \text{ kJ}$$

4. What is the change in enthalpy for this process?

$\Delta H = q$ because pressure is constant.

$$\Delta H = +47.9644 \text{ kJ}$$

5. What is the change in entropy of the system for this process?

Work:

$$\Delta S_{\text{sys}} = \Delta S_{\text{vap}} + \Delta S_{\text{warm}}$$

$$\Delta S_{\text{sys}} = \frac{n\Delta H_{\text{vap}}}{T} + nC_{\text{gas}} \ln\left(\frac{T_f}{T_i}\right)$$

$$\Delta S_{\text{sys}} = \frac{(4\text{mol})(5560 \frac{\text{J}}{\text{mol}})}{77\text{K}} + (4\text{mol})(29.1 \frac{\text{J}}{\text{molK}}) \ln\left(\frac{298\text{K}}{77\text{K}}\right)$$

$$\Delta S_{\text{sys}} = 446.3 \frac{\text{J}}{\text{K}}$$

6. What is the change in entropy of the surrounding for this process?

Work:

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = \frac{-q_{\text{sys}}}{T}$$

$$\Delta S_{\text{surr}} = \frac{-47.9644 \text{ kJ}}{298\text{K}}$$

$$\Delta S_{\text{surr}} = -0.16095 \frac{\text{kJ}}{\text{K}} = -160.95 \frac{\text{J}}{\text{K}}$$

7. What is the total change in entropy (change in entropy of universe) for this process?

$$\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 446.3 \text{ JK}^{-1} - 160.95 \text{ JK}^{-1} = 285.35 \text{ JK}^{-1}$$

8. Does the thermodynamic calculation predict the observation that this process is spontaneous?

Yes. The change in entropy for the universe is positive which indicates that this is a spontaneous process.