Department of Chemistry
University of Texas at Austin

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Thermodynamics Unit - RAQ

Part I
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.

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

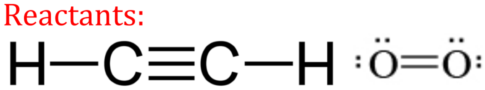
Multiple Bond Energies (kJ/mol of bonds)

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

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

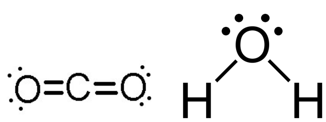
$C_2H_2(g) + (5/2)O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$

Then, draw the structures for each species:
Reactants:



Two C-H bonds, one C≡C bond and one O=O bond

Products:



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

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

$$\Delta H = [1(2x413) + 1(1x835) + \frac{5}{2}(1x498)] - [2(2x799) + 1(2x463)]$$

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

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:

ΔH = +[Bond Energy of Reactants] + –[Bond Energy of Products]

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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:

$C_2H_2(g) + (5/2)O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$

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

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

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

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

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:

$C_2H_2(g) + (5/2)O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$

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

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

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

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

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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?

Since both ΔH and ΔS are negative, this reaction will have a temperature dependence. A negative ΔH is working toward spontaneity (toward a negative ΔG). A negative ΔS is working against spontaneity (against a negative ΔG), so in order for this reaction to be spontaneous, we need to minimize the TΔS term. In order for this reaction to be non-spontaneous, we need to maximize the TΔS term. So At low temperatures the reaction will be spontaneous and at high temperatures the reaction will be non-spontaneous. We can calculate the temperature at which the reaction switches from spontaneous to non-spontaneous.

Work:

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

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

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

$$Temp\ where\ non-spont:$$

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

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

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

Non-spontaneous when T > 6032 K

5. Imagine this reaction was run at constant pressure and temperature, what is the work for this process (combustion of 4 g C_2H_2)?

$C_2H_2(g) + (5/2)O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$

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

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

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

$$For\ 4g:$$

$$w_{4g} = 3716\frac{J}{molrxn}(\frac{1molrxn}{1molC_2H_2})(\frac{1molC_2H_2}{26gC_2H_2})(4gC_2H_2)$$

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

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 C_2H_2)?

$\Delta U = q + w$
At constant pressure $\Delta H = q_p$

$\Delta U = \Delta H + w$

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

$$\Delta H_{4g} = -1300 \frac{kJ}{molrxn}\left(\frac{1molrxn}{1molC_2H_2}\right)\left(\frac{1molC_2H_2}{26gC_2H_2}\right)(4gC_2H_2)$$

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

$$\Delta U = q + w$$

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

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 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.

$\Delta U = q_{sys} = -q_{surroundings} = -(q_{cal} + q_{water})$
$\Delta U = -(C_{cal}\Delta T + m_{water}C_{water}\Delta T)$
$\Delta U = -\Delta T(C_{cal} + m_{water}C_{water})$
$-199.4\ kJ = -\Delta T[3.51 kJ^{\circ}C^{-1} + (2000g)(0.004184\ kJg^{-1}{}^{\circ}C^{-1})]$
$\Delta T = -199.4\ kJ \div -11.88\ kJ^{\circ}C^{-1}$
$\Delta T = 16.8^{\circ}C$

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Part II
PHYSICAL CHANGE:

$$N_2(liq,77K) \longrightarrow N_2(gas,298K)$$

$\Delta H^0_{vaporization} = 5.56 \text{ kJ mol}^{-1}$

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

$T_b = 77$ K

$T_{surr} = 298$ K

1. How much heat is absorbed during this change given 4 moles of N_2?

Work:

$$q = n\Delta H^\circ_{vap} + nC_{gas}\Delta T$$

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

$$q = 47.9644 \ kJ$$

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

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

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

$\Delta U = q + w = 47.96$ kJ – 9.91 kJ = +38.05 kJ

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

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

$\Delta H = +47.9644$ kJ

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

Work:

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

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

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

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

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

Work:

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

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

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

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

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

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.