Thermochemistry

- Petrucci, Harwood and Herring: Chapter 7

Thermochemistry

- The study of energy in chemical reactions
- A sub-discipline of thermodynamics

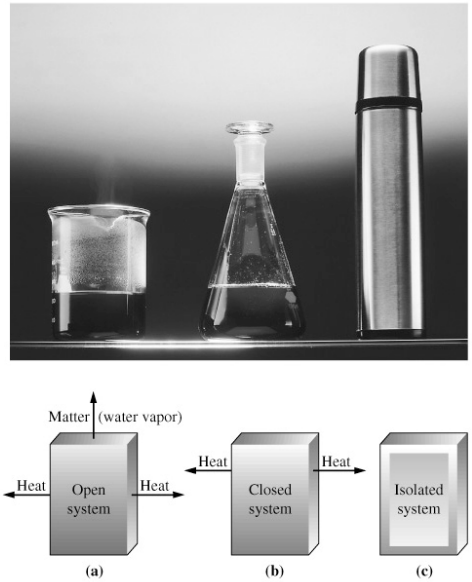
- Thermodynamics studies the bulk properties of matter and deduces a few general laws
  - It does not require any knowledge/assumptions of molecules

Definitions

- System
  - The part of the universe we chose to study
- Surroundings
  - The rest of the universe (normally we only worry about the immediate surroundings)
- Process
  - A physical occurrence (usually involving energy flow)

Additional definitions

- Open system
  - A system where energy and matter can be exchanged with the surroundings
- Closed system
  - A system where energy but not matter can be exchanged with the surroundings
- Isolated system
  - A system where neither energy nor matter can be exchanged with the surroundings



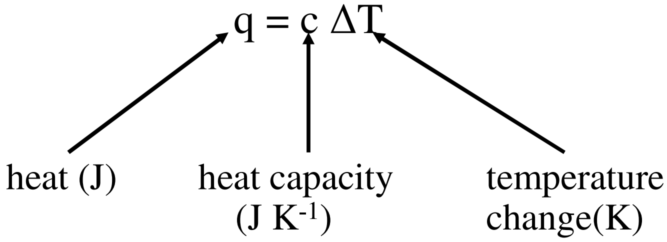
Systems and Energy

- All systems will contain energy
  - In thermodynamics we are interested in the flow of energy, particularly in the forms of heat and work.
  - Note that heat and work occur when there is a process. They only exist when something happens.
    - The system has energy, (often described as the capacity to do work), it does not have heat or work.

Heat

- Heat
  - – Energy that is transferred between a system and its surroundings as a result of temperature differences
  - – Heat transfer can change the temperature of something but it does not always do (only) that
  - – Heat transfer can melt or vaporize material

- In the case of a material that does not change phase, the increase in temperature of a system ΔT due to the input of a given amount of heat q is given by



$$q = c\ \Delta T$$

heat (J)

heat capacity ($J\ K^{-1}$)

temperature change(K)

- The heat capacity is a constant that depends on the system. So it’s not particularly useful.
- It is better to be able to define heat capacity in terms of a particular compound

$q = nC\Delta T$

Number of moles

molar heat capacity (J K^{-1} mol^{-1})

$q = mc\Delta T$

mass (kg)

specific heat (J K^{-1} kg^{-1})

Units

- The SI unit of heat is a Joule (since it is an energy)
- The older unit of heat is the calorie which is defined as the heat required to raise the temperature of 1 g of water 1^{O}C

1cal = 4.184 J

Sign convention and conservation of energy

- When heat flows between a system and its surroundings, we define:

  q to be positive if heat is supplied to the system

  q to be negative if heat is withdrawn from the system

- If there are no phase changes, conservation of energy requires that

$$q_{system} + q_{surroundings} = 0$$

or

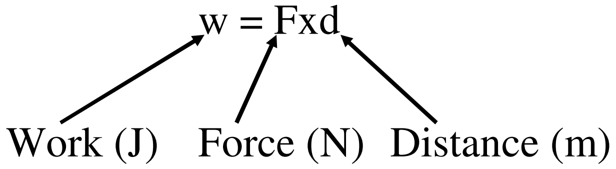
$$q_{system} = -q_{surroundings}$$

Work

- Often when a chemical reaction occurs, work is done. (this is the principle of an engine)
- Since work and heat are both forms of energy we must consider both.

Work

- Work is done when a force acts through a distance. For example when a mass is moved.
- Definition



$$w = Fxd$$

Work (J) Force (N) Distance (m)

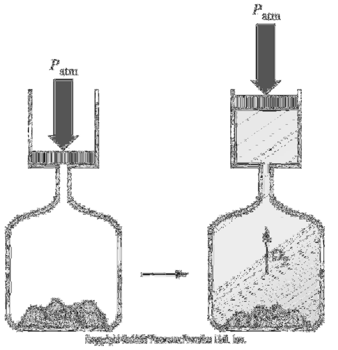
- The same definitions apply for work as for heat:

w is positive if work is done on the system
w is negative if work is done by the system

Pressure-Volume Work

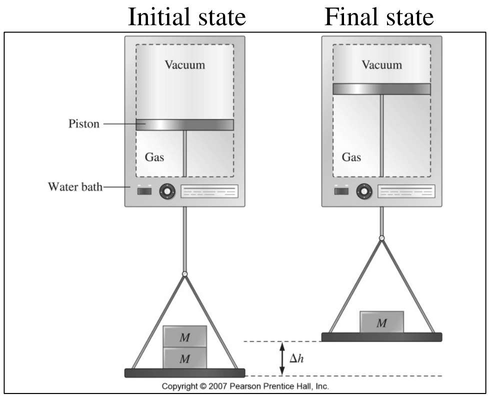
This is the most common type of work.

For example, a gas formed in a reaction pushes against the atmosphere causing a volume change.



(Note that because the gas is expanding, the system is doing work on the surroundings, so work must be negative.)

Pressure-Volume Work



$$w = -F \times d$$

$$= -(M \times g) \times \Delta h$$

$$= \frac{-(M \times g)}{A} \times \Delta h \times A$$

$$= -P\Delta V$$

The gas is expanding in this process so the system is doing work on the surroundings and therefore it is negative.

Note: Derivation assumes that the piston and pan assembly is massless and the water bath keeps the temperature of the gas constant.

Calculating Pressure-Volume Work

Suppose the gas in the previous figure is 0.100 mol He at 298 K and the each mass in the figure corresponds to an external pressure of 1.20 atm. How much work, in Joules, is associated with its expansion at constant pressure?

Assume an ideal gas and calculate the volume change:

$V_i = nRT/P$

$= (0.100\text{ mol})(0.08201\text{ L atm mol}^{-1}\text{ K}^{-1})(298\text{K})/(2.40\text{ atm})$

$= 1.02\text{ L}$

$V_f = 2.04\text{ L}$

$\Delta V = 2.04\text{ L} - 1.02\text{ L} = 1.02\text{ L}$

Calculate the work done by the system:

$w = -P\Delta V$

$= -(1.20\text{ atm})(1.02\text{ L})\left(\frac{101\text{ J}}{1\text{ L atm}}\right)$

$= -1.24 \times 10^2\text{ J}$

A negative value signifies that work is done ON the surroundings

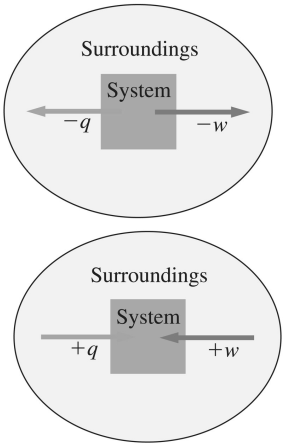
Where did the conversion factor come from?

Compare two versions of the gas constant and calculate.

8.3145 J/mol K = 0.082057 L atm/mol K

(8.3145 J/mol K)/(0.082057 L atm/mol K) = 101.33 J/L atm

First Law of Thermodynamics



- We have defined a system, work and heat.
- A closed system can exchange heat and work with its surroundings.
- The system has some energy we call the internal energy, U.

First Law of Thermodynamics

- The first law of thermodynamics

$$\Delta U = q + w$$

The internal energy is a **state function**. This means that its value depends on the state of the system (its pressure, temperature etc) not on how it got there.

Heat and work are not state functions. Their values depend on where the system has been, not on where it is.

Where is the internal energy?

- It is not necessary that we know where the internal energy resides, But:
- It can be energy due to motion in the molecules e.g. translational energy (kinetic), or energy due to molecular rotational and vibration.
- For an ideal gas the internal energy is the kinetic energy

$$E = \frac{3RT}{2}$$

Thermochemistry and the First Law

We have $\Delta U = q + w$

(For chemical reactions, the most common form of heat is the heat of reaction q_{rxn}.)

For a constant volume process:

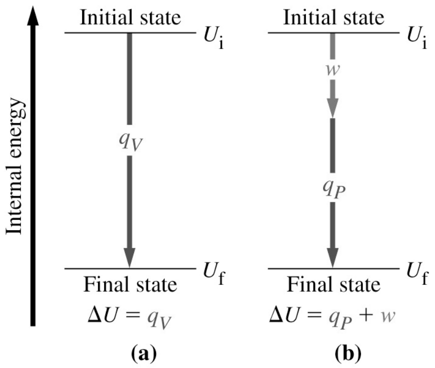
$$\Delta U = q + w = q - P\,\Delta V$$

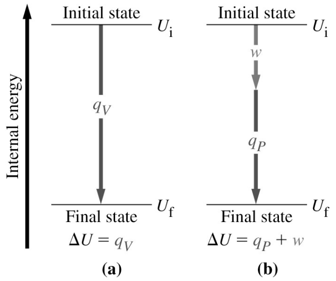
But $\Delta V = 0$ therefore $\Delta U = q_v$

The subscript indicates a constant volume process.

More reactions occur at constant pressure conditions than constant volume. In this case the volume of the system can change and work can be done.

Suppose the system has to change from one state to another. It can do it at constant volume or constant pressure but the heat involved is different





$$q_v = q_p + w$$

But $q_v = \Delta U$ and $w = -P\,\Delta V$

So

$$\Delta U = q_p - P\,\Delta V$$
$$q_p = \Delta U + P\,\Delta V$$

U, P and V are state functions so a combination of them will also be a state function.

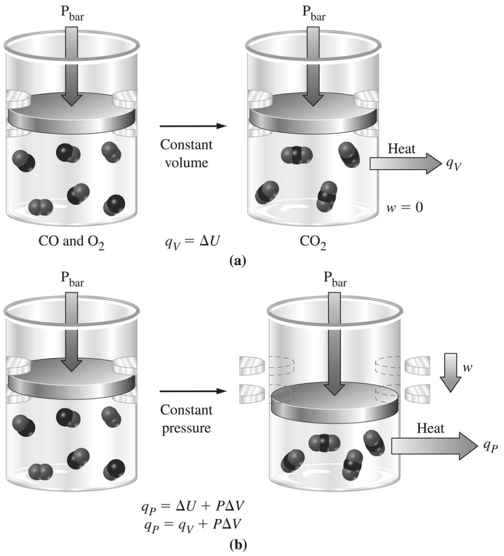
Define **enthalpy** as: **$H = U + PV$**

$$\Delta H = \Delta U + \Delta PV$$

At constant pressure

$$\Delta H = \Delta U + P\Delta V \text{ so } \Delta H = q_p$$

$$2\,CO(g) + O_2(g) \rightarrow 2\,CO_2(g)$$



At constant volume

$\Delta U = q_v = -563.5$ kJ

At constant pressure, work is done on the system. You get the heat from reaction and from the work.

$\Delta H = q_p = -566.0$ kJ

Enthalpy and change of state

- There is usually a flow of heat when there is a change of state (solid to liquid, liquid to vapour)
- This is usually expressed as the enthalpy of fusion or enthalpy of vaporization. E.g.

$H_2O(s) \rightarrow H_2O(l) \qquad \Delta H = 6.01 \text{ kJ mol}^{-1}$

$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H = 44.0 \text{ kJ mol}^{-1}$

- This is often just called the heat of fusion or heat of vaporization.

Enthalpy/thermochemistry

- Thermochemistry is the branch of thermodynamics that deals with energy changes in chemical reactions.
- Normally a chemical reaction is expressed with the associated enthalpy stated

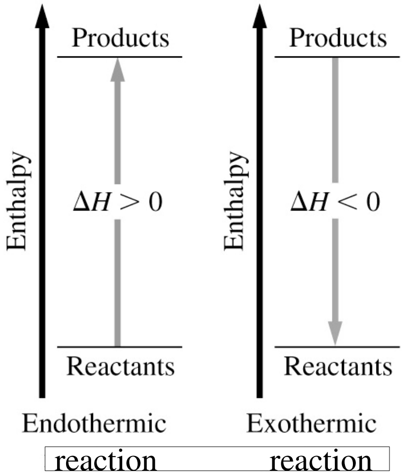
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H^\circ = -285.83 \text{ kJ}$

exothermic

Standard conditions

{P = 1 bar, T must be specified

(usually 298K)}



Hess's Law

Enthalpy is a state function. Therefore we can can use some obvious properties to determine unknown enthalpies.

1. Enthalpy changes are proportional to the amount of material.
2. The sign of the enthalpy changes if a reaction is reversed.
3. (Hess's Law) If a reaction can be thought of as proceeding through a number of steps, then the enthalpy change on reaction must be the sum of the enthalpy changes for each step.

For

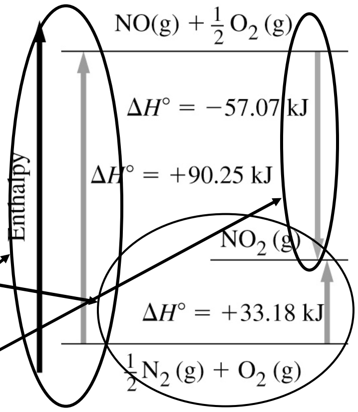
$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)$

We can think of the reaction proceeding as written

Or in two steps

$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO(g) + \frac{1}{2}O_2$

$NO(g) + \frac{1}{2}O_2 \rightarrow NO_2\ (g)$



$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g) \qquad \Delta H = +90.25\ kJ\ mol^{-1}$

$NO(g) + \frac{1}{2}O_2 \rightarrow NO_2\ (g) \qquad \Delta H = -57.07\ kJ\ mol^{-1}$

$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g) \qquad \Delta H\ +33.18\ kJ\ mol^{-1}$

Standard enthalpies of formation

- We have seen that the enthalpy of a reaction is calculated as a difference between the enthalpies of the products and reactants.
- We do not have an absolute scale for enthalpies (what is the enthalpy of O_2? For example)
- Just as we measure heights above sea-level, we measure enthalpies with respect to the standard state.

Standard State

- By definition: the enthalpy of an element in its most stable form at a pressure of 1 bar for a specified temperature is zero. (usually tabulated for 298K)
- E.g. O_2(g), Br_2(l), C(graphite), Na(s)…
- We calculate all enthalpies from this standard state

- We can now define a standard enthalpy of formation as the enthalpy change that occurs in the formation of one mole of the substance from its elements in their standard states.
- Usually given the symbol ΔH_f^o where the f is for formation and the ^{o} indicates standard conditions.

- Examples of standard enthalpies of formation

$C(gr) + ½O_2(g) \rightarrow CO(g)$ $\Delta H_f^o(CO(g))=-110.5\ kJ\ mol^{-1}$

$½H_2(g) + ½F_2(g) \rightarrow HF(g)$ $\Delta H_f^o(HF(g))=-271.1\ kJ\ mol^{-1}$

$½N_2(g) + ½O_2(g) \rightarrow NO(g)$ $\Delta H_f^o(NO(g))= + 90.25\ kJ\ mol^{-1}$

- Now we have standard enthalpies of formation we can determine the enthalpy of a reaction.

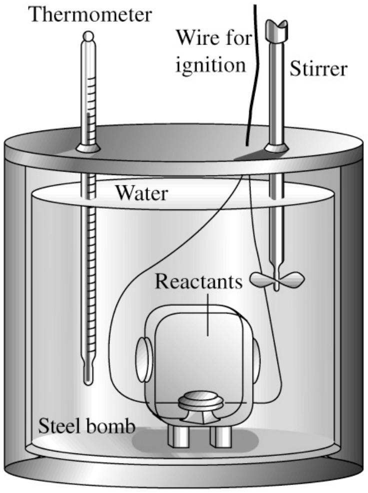
$$\Delta H_{\text{reaction}} = H_{\text{products}} - H_{\text{reactants}}$$

$$= \sum \nu_p \Delta H_f^o(\text{products}) - \sum \nu_r \Delta H_f^o(\text{reactants})$$

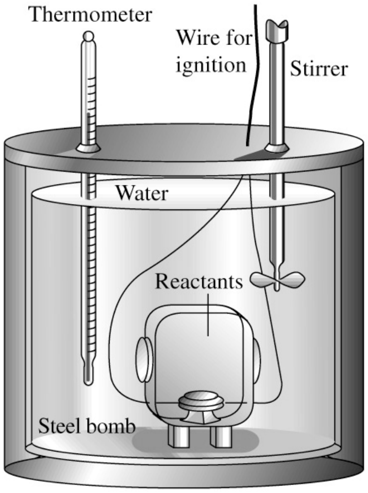
where Σ is a sum over the standard enthalpies of formation ΔH_f^o multiplied by their stoichiometric coefficients ν.

Where do ΔH_f^o values come from?

- All enthalpies of formation can be traced to calorimetry experiments.
- Most widely used is the bomb calorimeter



- The bomb calorimeter is a constant volume reactor, usually used for combustion reactions.
- The reagents are the system and the calorimeter is the surroundings.
- By measuring the heat transferred into the surroundings the heat of the reaction can be determined.



- If the increase in temperature of the surroundings is ΔT then the heat going into the surroundings is

$$q_{calorimeter} = c\ \Delta T$$

Since the reaction takes place at constant volume

$$\Delta U = q_{rxn} = -\ q_{calorimeter} \quad \text{(converted to per mole)}$$

To get ΔH_{rxn} we use

$$\Delta H_{rxn} = \Delta U + \Delta PV$$

And the ideal gas law

$$\Delta H_{rxn} = \Delta U + \Delta nRT$$

Then we use

$$\Delta H_{rxn} = \sum \nu_p \Delta H_f^o(\text{products}) - \sum \nu_r \Delta H_f^o(\text{reactants})$$

Example:

Calculate the standard heat of formation of CH_4 if a bomb calorimeter experiment at an initial temperature of 298K gives a measured heat gain in the calorimeter of 885.4 kJ per mole of CH_4.

The combustion reaction is the one that fully oxidizes the reagents:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta U = q_{rxn} = - q_{calorimeter} = -885.4 \text{ kJ mol}^{-1}$$

$$\Delta H_{rxn} = \Delta U + \Delta nRT$$

$\Delta n = 1\text{-}3 = -2$

$$\Delta H_{rxn} = -885.4 + (-2)\text{x}8.314\text{x}298\text{x } 10^{-3} \text{ kJ mol}^{-1}$$

$$= -890.4 \text{ kJ mol}^{-1}$$

$$\Delta H_{rxn} = \sum \nu_p \Delta H_f^o(\text{products}) - \sum \nu_r \Delta H_f^o(\text{reactants})$$

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$$

$$\Delta H_{rxn} = \sum \nu_p \Delta H_f^o(\text{products}) - \sum \nu_r \Delta H_f^o(\text{reactants})$$

$$\Delta H_{rxn} = \Delta H_f^o(CO_2) + 2\Delta H_f^o(H_2O) - \Delta H_f^o(CH_4)$$

If we know the heats of formation of CO_2 and H_2O then:

$$\Delta H_{rxn} = \Delta H_f^o(CO_2) + 2\Delta H_f^o(H_2O) - \Delta H_f^o(CH_4)$$

$$-890.4 = -393.51 + 2\times(-285.85) - \Delta H_f^o(CH_4)$$

$$\Delta H_f^o(CH_4) = -74.8 \text{ kJ mol}^{-1}$$

Bond Energies

- The Bond Dissociation Energy is the energy to break a mole of bonds.

$H_2(g) \rightarrow 2H(g) \qquad \Delta H = BE(H\text{-}H) = +435.93\ kJ\ mol^{-1}$

- For cases where there are more than one identical bond, the average is taken

$H_2O(g) \rightarrow H(g) + OH(g) \quad \Delta H = BE(H\text{-}OH) = +498.7\ kJ\ mol^{-1}$

$OH(g) \rightarrow H(g) + O(g) \qquad \Delta H = BE(H\text{-}O) = +428.0\ kJ\ mol^{-1}$

$BE(HO\ in\ H_2O) = +463.4\ kJ\ mol^{-1}$

Bond Energies

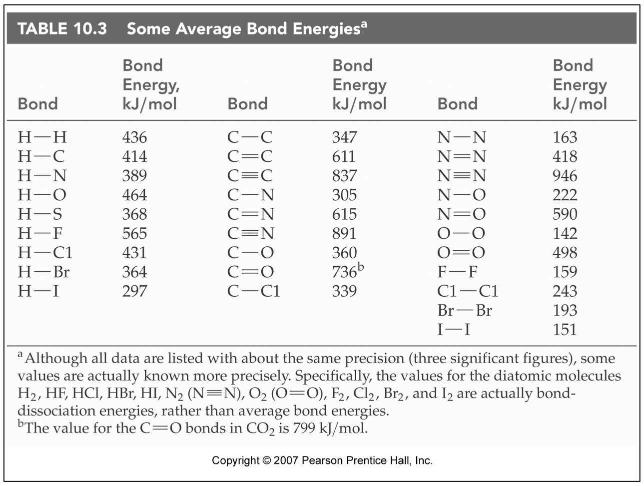


TABLE 10.3 Some Average Bond Energies[a]

Bond	Bond Energy, kJ/mol	Bond	Bond Energy kJ/mol	Bond	Bond Energy kJ/mol
H—H	436	C—C	347	N—N	163
H—C	414	C═C	611	N═N	418
H—N	389	C≡C	837	N≡N	946
H—O	464	C—N	305	N—O	222
H—S	368	C═N	615	N═O	590
H—F	565	C≡N	891	O—O	142
H—C1	431	C—O	360	O═O	498
H—Br	364	C═O	736[b]	F—F	159
H—I	297	C—C1	339	C1—C1	243
				Br—Br	193
				I—I	151

[a] Although all data are listed with about the same precision (three significant figures), some values are actually known more precisely. Specifically, the values for the diatomic molecules H_2, HF, HCl, HBr, HI, N_2 (N≡N), O_2 (O═O), F_2, Cl_2, Br_2, and I_2 are actually bond-dissociation energies, rather than average bond energies.

[b] The value for the C═O bonds in CO_2 is 799 kJ/mol.

Bond Energies

- Hess's law can be used to show

$\Delta H_{rxn} = \Delta H(\text{bond breakage}) - \Delta H(\text{bond formation})$

$\Delta H_{rxn} = \Sigma\ BE(\text{reactants}) - \Sigma\ BE(\text{products})$

This will never be as precise as using heats of formation as BEs are always averages.

Bond Energy Examples

1) **Example 10-15 pg 409**

Calculate ΔH_{rxn} for the reaction

$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$

- draw each molecule and its bonds to emphasize which bonds are broken and which ones are formed (could break all bonds in reactants and then form all of the bonds in the products, but this is not necessary)
- one C-H bond and one Cl-Cl bond are broken; one C-Cl bond and one H-Cl bond are formed

$$
\begin{aligned}
\Delta H_{rxn} &= \Delta H(\text{bonds broken}) + \Delta H(\text{bonds formed}) \\
&= \{BE(C\text{-}H) + BE(Cl\text{-}Cl)\} - \{BE(C\text{-}Cl) + BE(H\text{-}Cl)\} \\
&= \{414\text{ kJ} + 243\text{ kJ}\} - \{339\text{ kJ} + 431\text{ kJ}\} \\
&= -113\text{ kJ}
\end{aligned}
$$

2) Practice Problem - estimate versus experiment

Calculate ΔH_{rxn} for the reaction

$$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$$

- note that it is important to know the bond order
- one N≡N triple bond and 3 H-H single bonds are broken; 6 N-H single bonds are formed (sketch if necessary)

ΔHrxn = ΔH(bonds broken) + ΔH(bonds formed)
= {BE(N≡N) + 3 BE(H-H)} - {6 BE(N-H)}
= +946 kJ + 3(436 kJ) - 6(389 kJ)
= -80 kJ

Note: experimentally ΔH_{rxn} determined to be -92 kJ