
Chapter 6. Thermochemistry

1. Terms to Know:

- thermodynamics
- thermochemistry
- energy
- kinetic energy
- potential energy
- heat
- heat vs. temperature
- work
- work of expanding gases
- work of expanding gases under constant pressure
- internal energy
- system
- surroundings

2. Units

Joule (J) 1 J =

calorie (cal) 1 cal =

Calorie (Cal) 1 Cal =

3. The First Law of Thermodynamics

First Law: 1)

2)

3)

Algebraic expression of the first law:

$\Delta E =$

where $\Delta E =$

$\Delta E =$

q =

w =

4. Sign Convention--very important.

The signs of q and w are determined from the point of view *of the system*.

If q is positive, then

If q is negative, then

If w is positive, then

If w is negative, then

Important: if you are describing the *change* in energy (ΔE) or *change* in enthalpy (ΔH), you must give the sign. However, if you are asked for the amount of energy (or heat) added or removed, then you report the magnitude (or absolute value).

$\Delta X =$

$\Delta S =$

Endothermic--

Exothermic--

Example: A substance gains 25 J of heat and does 30 J of work. What is the ΔE for this system?

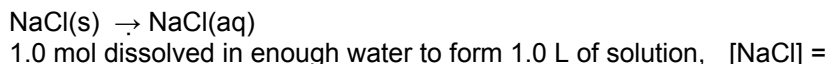
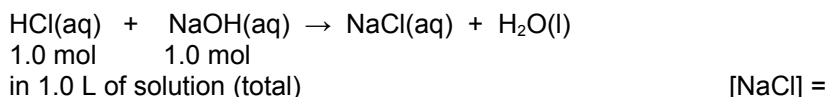
5. State Function

Definition of State Function: A property of a system that is determined by specifying _____

• The value of a state function does not depend on the _____ of the system, or the _____ followed, only on its _____.

• Some examples of state functions:

• Example:



• Some examples of quantities which are not state functions:

• Example of a battery: $\Delta E = q + w$

discharged in a flashlight:

discharged in a toy car:

In both processes (flashlight and car), $\Delta E =$

6. Enthalpy (H)

Derivation of an Important Relationship:

start with the second law: $\Delta E =$

solve for q: $q =$

Under constant volume conditions, _____,

and $q_v =$

where q_v means:

Many chemical reactions occur in open containers under _____ conditions.

expansion work under constant pressure: $w =$

so under constant pressure conditions:
(plug $-P\Delta V$ into the equation) $q_p =$

where q_p means:

Now we define the thermodynamic property $\Delta H =$

where $H =$

$$\Delta H =$$

$$\text{or } \Delta H =$$

$$\Delta E =$$

$$P\Delta V =$$

At constant pressure the change in enthalpy, ΔH , equals the energy flow as heat (or the heat of reaction).

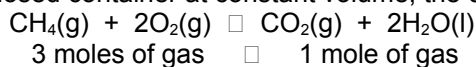
- If you have a constant pressure reaction, you can measure the heat consumed by the reaction or the heat produced by the reaction, and that is equal to the change in enthalpy.
- H is a state function; ΔH is a state function.

if $\Delta H > 0$ then the reaction is _____

if $\Delta H < 0$ then the reaction is _____

- Example of a reaction not under constant pressure:

In an enclosed container at constant volume, the combustion of methane (CH_4)



3 moles of gas \rightarrow 1 mole of gas

Therefore the pressure *decreases*, and the measured heat is *not* the enthalpy change.

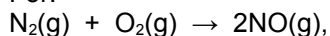
Question: What are two important differences between ΔH and q ?

Answer: (1)

(2)

7. Thermochemical Equations

For:



this reaction is found to be endothermic:

Thermochemical equation:

Important! The stoichiometric coefficients in a thermochemical equation refer to

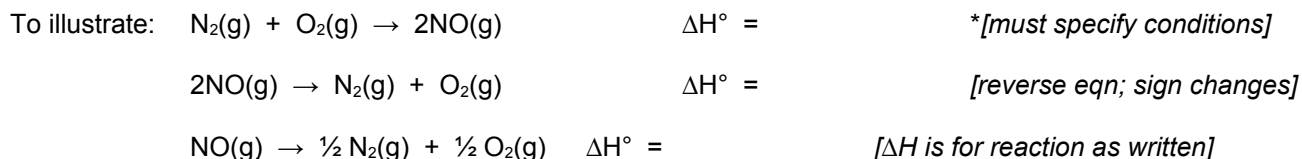
Three rules for thermochemical equations:

- 1) The conditions must _____

Shortcut:

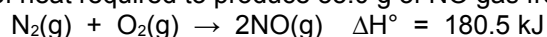
- 2) When the reaction is reversed, _____

- 3) The enthalpy change, ΔH , is for _____

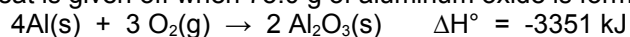


*The first equation means that when 1 mol of N_2 reacts with 1 mol of O_2 to form 2 mol of $\text{NO}(\text{g})$, the enthalpy change is +180.5 kJ *when it is measured under standard conditions.*

Example: What is the amount of heat required to produce 55.0 g of NO gas from N_2 and O_2 ?



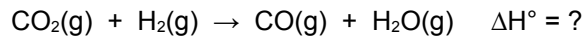
Example: How much heat is given off when 75.0 g of aluminum oxide is formed from aluminum and oxygen?



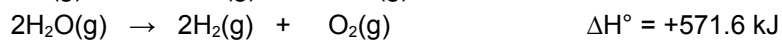
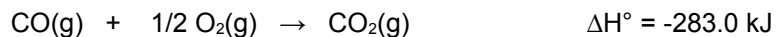
8. Hess's Law

Hess's Law states:

Example problem: Use Hess's law to calculate ΔH° for the reaction



from the following thermochemical equations:



9. Enthalpies of Formation

A formation reaction:

Standard enthalpy of formation:

Example: for $\text{CO}(\text{g})$, $\Delta H^\circ_f = -110.5 \text{ kJ/mol}$. Write the corresponding thermochemical equation.

Important: Sometimes fractional coefficients are _____.

Example: for $\text{KClO}_3(\text{s})$, $\Delta H^\circ_f = -397.73 \text{ kJ/mol}$. Write the corresponding thermochemical equation.

Question: Which substances always have zero as their standard enthalpy of formation?

Why?

As a consequence of Hess's law, we can use ΔH°_f values to calculate the ΔH°_{rxn} :

$$\Delta H^\circ_{rxn} =$$

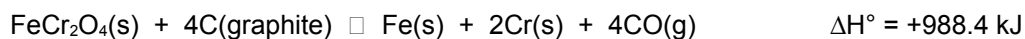
where n_p and n_r represent the _____

Just remember: _____ minus _____

Example: Use the following standard enthalpies of formation to calculate the standard molar enthalpy of combustion of glucose ($C_6H_{12}O_6$).

substance	ΔH°_f
$C_6H_{12}O_6(s)$	-1260
$CO_2(g)$	-393.5
$H_2O(l)$	-285.8

Example: The chromium metal used in chrome steel is obtained by heating the ore chromite ($FeCr_2O_4$) with carbon:



Given that the standard enthalpy of formation of carbon monoxide is -110.5 kJ/mol , calculate the standard enthalpy of formation of $FeCr_2O_4$.

10. Calorimetry

Heat capacity

Specific heat capacity (c)

Important: $q =$

Molar heat capacity (C)

Example: How many joules of heat must be removed from 100 g of Hg to cool it from 20°C to its freezing point of -39°C ? (specific heat of Hg = $0.140 \text{ J/g}\cdot^\circ\text{C}$)

Question: Given this table of specific heats:

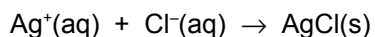
Pb	$0.128 \text{ J/g}\cdot^\circ\text{C}$
Al	$0.902 \text{ J/g}\cdot^\circ\text{C}$
H_2O	$4.18 \text{ J/g}\cdot^\circ\text{C}$

100 g each of Pb, Al, and H_2O are placed in the sun for one hour. They all absorb an equivalent amount of heat from the sun. Which one has the highest temperature?

Example: A 30.0 g sample of water at 280. K is mixed with 50.0 g of water at 330. K. Calculate the final temperature of the mixture assuming no heat loss to the surroundings.

Example: A 50.0 g chunk of lead is heated to 100.0°C and then dropped into a beaker with 100.0 g of H₂O at 25.0° C. Assuming that no heat is lost to the surroundings, determine the final solution of the mixture. (The specific heat of water is 4.18 J/g·°C; the specific heat of lead is 0.128 J/g·°C.)

Example: In a coffee-cup calorimeter, 150.0 mL of 0.100 M AgNO₃ and 50.0 mL of 0.100 M HCl are mixed to yield the following reaction:



The two solutions were initially at 22.60°C, and the final temperature is 23.40°C. Calculate the heat that accompanies this reaction in kJ/mol of AgCl formed. Assume that the combined solution has a mass of 100.0 g and a specific heat capacity of 4.18 J/g·°C.

Example: The specific heat of aluminum is 0.902 J/g·°C. Calculate the molar heat capacity of aluminum.