

Understanding Heats of Reaction -

thermodynamics is the science of the relationships between heat and other forms of energy. *Thermochemistry* refers to the heat absorbed or evolved during a chemical reaction.

Law of Conservation of Energy

Energy can be converted from one form to another but can neither be created nor destroyed.

 $(E_{universe} \text{ is constant})$

Energy

• Energy is defined as *the capacity to move matter*.

Energy can be in many forms:

- >Radiant Energy -Electromagnetic radiation.
- >Thermal Energy Associated with random motion of a molecule or atom.
- >Chemical Energy Energy stored within the structural limits of a molecule or atom.



A solar-powered water pump has photovoltaic cells that protrude from top panels. These cells collect energy from sunlight, storing it momentarily in a battery, which later runs an electric motor that pumps water up to a storage tank on a hill. What energy conversions are involved in using sunlight to pump water into the storage tank? Energy and Its Units - energy is the potential or capacity to move matter

1 Kinetic energy. $E_k = \frac{1}{2} \text{ mv}^2$ SI unit of energy is the joule (J) which has units kg \cdot m²/s². 1 calorie (cal) is equal to the amt of heat necessary to raise 1 g of H₂O by 1 °C. 1 cal = 4.184 J







- **Potential Energy**: This energy depends on the "position" (such as height) in a "field of force" (such as gravity).
- For example, water of a given mass *m* at the top of a dam is at a relatively high "position" *h* in the "gravitational field" *g* of the earth.

 $E_p = mgh$

A Problem to Consider

• Consider the potential energy of 1000 lb of water (453.6 kg) at the top of a 300 foot dam (91.44 m).

 $E_{p} = (453.6 \text{ kg}) \times (9.80 \text{ m/s}^{2}) \times (91.44 \text{ m})$ $E_{p} = 4.06 \times 10^{5} \text{ kg} \cdot \text{m}^{2} / \text{s}^{2}$ $E_{p} = 4.06 \times 10^{5} \text{ J}$

Energy • **Internal Energy** is the energy of the *particles making up a substance*.

• The *total energy* of a system is the sum of its kinetic energy, potential energy, and internal energy, *U*.

 $\mathbf{E}_{\text{tot}} = \mathbf{E}_{\text{k}} + \mathbf{E}_{\text{p}} + \mathbf{U}$

First Law

First Law of Thermodynamics:

The energy of the universe is constant.

First Law

 $\Delta E = q + w$

 ΔE = change in system's internal energy q = heat w = work

Temperature v. Heat

Temperature reflects random motions of particles, therefore related to kinetic energy of the system.

Heat involves a transfer of energy <u>between</u> 2 objects due to a temperature difference



Work

work = force \times distance

since pressure = force / area,

work = $pressure \times volume$

 $w_{\text{system}} = -P\Delta V$ Where $\Delta V = V_{\text{final}} - V_{\text{initial}}$

First Law of Thermodynamics

·Both work & heat are ways in which energy can be transferred.

The way that energy transfer is divided between work and heat depends on the conditions of transfer - and is called the "pathway". However, the total amount of energy transferred (w + q) will always remain constant.

State Function

Depends only on the present state of the system - not how it arrived there.

It is independent of pathway.

Internal Energy is a State Function



Heat of Reaction

- Heat is defined as the energy that flows into or out of a system because of a difference in temperature between the system and its surroundings.
 - Heat flows from a region of higher temperature to one of lower temperature; once the temperatures become equal, heat flow stops.

System and Surroundings

System: That on which we focus attention

Surroundings: Everything else in the universe

Universe = System + Surroundings

Heat of Reaction

- In chemical reactions, heat is often transferred from the "system" to its "surroundings," or vice versa.
 - The substance or mixture of substances under study in which a change occurs is called the *thermodynamic system* (or simply *system*.)
 - The *surroundings* are everything in the vicinity of the thermodynamic system.





2. An endothermic process is a chemical reaction or physical change in which heat is absorbed (q is positive)











Exo and Endothermic

Heat exchange accompanies chemical reactions.

Exothermic: Heat flows out of the system (to the surroundings).

Endothermic: Heat flows into the system (from the surroundings).

Enthalpy and Enthalpy Change

- The heat absorbed or evolved by a reaction depends on the conditions under which it occurs the "pathway".
 - Usually, a reaction takes place in an open vessel, and therefore at the constant pressure of the atmosphere.
 - The heat of this type of reaction is denoted q_p, the heat at constant pressure.

Enthalpy and Enthalpy Change

- Enthalpy and Internal Energy
 - The internal energy of a system, U, is precisely defined as the heat at constant pressure plus the work done by the system:



 In chemical systems, work is defined as a change in volume at a given pressure, that is:



(if volume of system expands - it does work on surroundings)

Internal energy (U). The sum of kinetic & potential energies of the atoms making up a substance as well as the subatomic particles of each atom.

$$E_{Total} = E_k + E_P + U$$

C Enthalpy and Enthalpy Change

Enthalpy is a state function. A state function is a property of a system that depends only on its present state, which is determined by variables such as temperature and pressure, and is independent of any previous history of the system. Thus, changes in enthalpy, Δ H, depend only on the initial and final states of the system not on the path (or way) in which the final state is reached.

Enthalpy

Enthalpy = H = E + PV (all state functions) $\Delta E = \Delta H - \Delta (PV)$ $\Delta H = \Delta E + \Delta (P V)$

At constant pressure,

$$q_P = \Delta E + P\Delta V$$
, or
 $\Delta E = q_p - P\Delta V$

where $q_P = \Delta H$ at constant pressure, $\Delta E = U_f - U_i$ ΔH = energy flow as heat (at constant pressure)

Enthalpy and Enthalpy Change

- Enthalpy, denoted **H**, is an extensive property of a substance that can be used to obtain the heat absorbed or evolved in a chemical reaction.
 - An extensive property is one that depends on the quantity of substance. (other examples - volume, mass, energy). An intensive property does not depend on amount of substance - e.g. temperature, vapor pressure.
 - Enthalpy is also a state function, a property of a system that depends only on its present state and is independent of any previous history of the system.



 $\Delta H = H(products) - H(reactants)$ = q_p (at constant pressure)

So ΔH is essentially the heat evolved or absorbed by the system (reaction) in an open vessel where the work portion of ΔU is unmeasured.





Measuring Heats of Reaction

- To see how **heats of reactions** are measured, we must look at the heat required to raise the temperature of a substance, because a thermochemical measurement is based on the relationship between heat and temperature change.
- The heat required to raise the temperature of a substance is its heat capacity.







Some Heat Exchange Terms

specific heat capacity, s

heat capacity per gram = J/°C g or J/K g $q = s m \Delta T$, where m is in g, $\Delta T = T_f - T_i$

molar heat capacity, C heat capacity per mole = J/°C mol or J/K mol $q = nC \Delta T$, where n = no. moles, $\Delta T = T_f - T_i$ Measurement of Heat of Reaction may be done using a calorimeter. A calorimeter is a device used to measure the heat absorbed or evolved during a physical or chemical change



Heats of Reaction: Calorimetry

- A calorimeter is a device used to measure the heat absorbed or evolved during a physical or chemical change. (see Figure 6.11)
 - The heat absorbed by the calorimeter and its contents is the negative of the heat of reaction.

 $\mathbf{q}_{\text{calorimeter}} = -\mathbf{q}_{\text{rxr}}$

A Problem to Consider A Problem to Consider • Suppose one mole of iron requires 6.70 J of • Calculate the heat absorbed by a heat to raise its temperature by one degree calorimeter when the temperature of 15.0 Celsius. The quantity of heat required to grams of water is raised from 20.0 °C to raise the temperature of the piece of iron 50.0 °C. (The specific heat of water is from 25.0 °C to 35.0 °C is: since $C \ge n =$ 4.184 J/g.ºC.) (6.70 J/mole C) x 1 mole $\mathbf{q} = \mathbf{s} \times \mathbf{m} \times \Delta^{T} \mathbf{I}$ $q = nC\Delta T = (6.70 J/^{\circ} C) \times (35.0 {^{\circ}C} - 25.0 {^{\circ}C})$ $\frac{J}{m^{\circ}C}$ × (15.0g) × (50.0 – 20.0°C) q = (4.184)q = 67.0 J $a = 1.88 \times 10^{3} J$

A Problem to Consider

• When 23.6 grams of calcium chloride, CaCl₂, was dissolved in water in a calorimeter, the temperature rose from 25.0 °C to 38.7 °C.

If the heat capacity of the solution and the calorimeter is 1258 J/°C, what is the enthalpy change <u>per mole</u> of calcium chloride?

Heats of Reaction: Calorimetry

- First, let us calculate the heat absorbed by the calorimeter.

 $q_{cal} = (1258 \text{ J/oC})(38.7 \text{ oC} - 25.0 \text{ oC})$



• Now we must calculate the heat per mole of calcium chloride.





Thermochemical Equations - the chemical equation for a reaction (including phase labels) in which the equation is given a molar interpretation, and the enthalpy of reaction for these molar amounts is written directly after the equation

2 Na (s) + 2 H₂O (l) \Rightarrow 2 NaOH (aq) + H₂ (g); Δ H = - 367.5 kJ

Applying Stoichiometry and Heats of Reactions

• Consider the reaction of methane, CH₄, burning in the presence of oxygen at constant pressure. Given the following equation, how much heat could be obtained by the combustion of 10.0 grams CH₄?

 $CH_{4}(g) + 2O_{2}(g) \rightarrow CO_{2}(g) + 2H_{2}O(1); \underline{\Delta}H^{\circ} = -890.3 \text{ kJ}$ $10.0 \text{ g } CH_{4} \times \frac{1 \text{ mol } CH_{4}}{16.0 \text{ g}} \times \frac{-890.3 \text{ kJ}}{1 \text{ mol } CH_{4}} = -556 \text{ kJ}$

Hess's Law

• Hess's law of heat summation states that for a chemical equation that can be written as the sum of two or more steps, the enthalpy change for the overall equation is the sum of the enthalpy changes for the individual steps. Hess's Law

Reactants \rightarrow Products

The change in enthalpy is the same whether the reaction takes place in one step or a series of steps.

Calculations via Hess's Law

1. If a reaction is reversed, ΔH is also reversed.

$$\begin{split} \mathrm{N}_2(g) \,+\, \mathrm{O}_2(g) \,&\rightarrow\, 2\mathrm{NO}(g) \quad \Delta H = 180 \ \mathrm{kJ} \\ 2\mathrm{NO}(g) \,&\rightarrow\, \mathrm{N}_2(g) \,+\, \mathrm{O}_2(g) \quad \Delta H = -180 \ \mathrm{kJ} \end{split}$$

2. If the coefficients of a reaction are multiplied by an integer, ΔH is multiplied by that same integer.

 $6NO(g) \rightarrow 3N_2(g) + 3O_2(g) \quad \Delta H = -540 \text{ kJ}$







 $2 S (s) + 2 O_2 (g) \longrightarrow 2.8O_2 (g) \Delta H = (-297 \text{ kJ}) x (2)$

 $2 SO_2(g) + O_2(g) \longrightarrow 2 SO_3(g) \Delta H = (198 kJ) x (-1)$

 $2 S (s) + 3 O_2 (g) \longrightarrow 2 SO_3 (g) \Delta H = -792 kJ$

We have multiplied the equation for the formation of sulfur dioxide by 2 and we have multiplied the heat of formation for sulfur dioxide by 2.

We have reversed the reaction for the formation of sulfur trioxide from sulfur dioxide and oxygen (and changed the sign for the corresponding heat of reaction)

We have added the reactions and the heats of reaction to obtain the values for the heat of formation of sulfur trioxide.

Standard Enthalpies of Formation

- The standard enthalpy of formation of a substance, denoted ΔH_{f^0} , is the enthalpy change for the formation of one mole of a substance in its standard state from its component elements in their standard state.
- Note **that** the standard enthalpy of formation for a pure element in its standard state is zero.

Standard States

Compound

For a gas, pressure is exactly 1 atmosphere.For a solution, concentration is exactly 1 molar.

Pure substance (liquid or solid), it is the pure liquid or solid.

Element

The form $[N_2(g), K(s)]$ in which it exists at 1 atm and 25°C.

ormula	∆H; (kJ/mol)	Formula	∆H; (kJ/mol)
e (g)	0	$C_2H_4(g)$	52.5
Hydrogen		$C_2H_6(g)$	-84.7
$H^{+}(aq)$	0	$C_6H_6(l)$	49.0
H(g)	218.0	HCHO(g)	-116
H ₂ (g)	0	CH3OH(l)	-238.6
Sodium		$CS_2(g)$	117
Na ⁺ (g)	609.8	CS2(1)	87.9
Na ⁺ (aq)	-239.7	HCN(g)	135
Na(g)	107.8	HCN(l)	105
Na(s)	0	CCL ₄ (g)	-96.0
NaCl(s)	-411.1	$CCl_4(I)$	-139
NaHCO ₃ (s)	-947.7	CH3CHO(g)	-166
Na ₂ CO ₃ (s)	-1130.8	C2H3OH(1)	-277.6
Calcium		Silicon	
Ca2+(aq)	-543.0	Si(x)	0
Ca(s)	0	$SiO_2(s)$	-910.9
CaO(x)	-635.1	$SiF_4(g)$	-1548
CaCO ₃ (x) (calcite)	-1206.9	Lead	
Carbon		Pb(x)	0
C(g)	715.0	PbO(s)	-219
C(graphite)	0	PbS(s)	-98.3
C(diamond)	1.9	Nitrogen	
CO(g)	-110.5	N(g)	473
CO ₂ (g)	-393.5	$N_2(g)$	0
HCO3"(aq)	-691.1	NH ₂ (g)	-45.9
CH ₄ (g)	-74.9		(continued)

What is AH ^o , for	Formula	∆Hį (kl/mol)	Formula	∆Hį (kJ/mol)
	NH4 ⁺ (aq)	-132.8	HF(g)	-273
	NO(g)	90.3	Chlorine	
HCl (aq)?	$NO_2(g)$	33.2	Cl ⁻ (aq)	-167.5
	HNO3(aq)	-206.6	Cl(g)	121.0
	Oxygen		$Cl_2(g)$	0
Remember that	O(g)	249.2	HCl(g)	-92.3
	O ₂ (g)	0	Bromine	
HCI is a strong acid	$O_3(g)$	143	Br ⁻ (g)	-218.9
and	OH ⁻ (aq)	-229.9	Br ⁻ (aq)	-120.9
	$H_2O(g)$	-241.8	$Br_2(l)$	0
$HCl(aq) \rightarrow H^+(aq) +$	H ₂ O(<i>l</i>)	-285.8	Iodine	
$C^{1-}(aq)$	Sulfur		I ⁻ (g)	-194.7
CI (aq)	S(g)	279	$\Gamma(aq)$	-55.9
	S ₂ (g)	129	$I_2(s)$	0
So to use the ΛH^0	S ₈ (rhombic)	0	Silver	
30 to use the $\Delta \Pi_{\rm f}$	S ₈ (monoclinic)	2	$Ag^{+}(g)$	1026.4
for Cl ⁻ (aq) and	SO ₂ (g)	-296.8	Ag ⁺ (aq)	105.9
$U^{+}(aq) (167.5 \text{ kI} +$	$H_2S(g)$	-20	Ag(s)	0
$\pi^{-10/.5}$ kJ +	Fluorine		AgF(s)	-203
0 kJ = -167.5 kJ	F (g)	-255.6	AgCl(s)	-127.0
	F (aq)	-329.1	AgBr(s)	-99.5
	F ₂ (g)	0	AgI(s)	-62.4



in the same physical state. Shown here two allotropes of S_8 , rhombic (left) and monoclinic (right). The rhombic form is more stable at room temperature and is the **reference form**.

Standard Enthalpies of Formation

• The **law of summation of heats of formation** states that the enthalpy of a reaction is equal to the total formation energy of the products minus that of the reactants.

$\Delta H^{o} = \sum n \Delta H^{o}_{f} (products) - \sum m \Delta H^{o}_{f} (reactants)$

 $\Box \Sigma$ is the mathematical symbol meaning "the sum of", and *m* and *n* are the coefficients of the substances in the chemical equation.

TABLE 6.2 Standard Enthalpies of Formation for Several Compounds at 25°C			
Compound	∆H° (kJ/mol)		
NH ₃ (g)	-46		
$NO_2(g)$	34		
$H_2O(l)$	-286		
$Al_2O_3(s)$	-1676		
$Fe_2O_3(s)$	-826		
$CO_2(g)$	-394		
$CH_3OH(l)$	-239		
$C_8H_{18}(l)$	-269		



• Large quantities of ammonia are used to prepare nitric acid according to the following equation:

 $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

- What is the standard enthalpy change for this reaction? Use Table 6.2 for data.



• You record the values of ΔH_f^{o} under the formulas in the equation, multiplying them by the coefficients in the equation.

$4\mathrm{NH}_3(\mathbf{g})$	$+50_{2}(g$	$) \rightarrow 4NO(g$	$(g) + 6H_2O(g)$
4(-45.9)	5(0)	4(90.3)	6(-241.8)
- You can values fo products	calculate or the reac	ΔH^{o} by subtra tants from the	cting the values for the

A Problem to Consider

• Using the summation law: $\Delta H^{\circ} = \sum n \Delta H_{f}^{\circ} (\text{products}) - \sum m \Delta H_{f}^{\circ} (\text{reactants})$ $\Delta H^{\circ} = [4(90.3) + 6(-241.8)] \text{ kJ} - [4(-45.9) + 5(0)] \text{ kJ}$ $\Delta H^{\circ} = -906 \text{ kJ}$ - Be careful of arithmetic signs as they are a likely source of mistakes.

Figure 6.10: A pathway for the combustion of ammonia.







 $C S_2$ is used in the manufacture of plastics and cellophane. Calculate ΔH° for the reaction below using the $\Delta H_{f^{\circ}}$ for the reactants and products shown below :

$$C S_{2} (g) + 3 O_{2} (g)$$

$$[1 m ol (87.9 kJ/m ol) + 3 m ol (0)]$$

$$C O_{2} (g) + 2 S O_{2} (g)$$

$$[1 m ol (-393.5 kJ/m ol) + 2 m ol(-296.8 kJ/m ol)$$

$$\Delta H^{\circ} = [\Sigma m \Delta H_{f^{\circ}} (products)] - [n\Delta H_{f^{\circ}} (reactan)]$$

$$= [(-393.5 kJ) + (-593.6 kJ)] - [87.9 kJ]$$

$$= -1075.0 kJ$$

