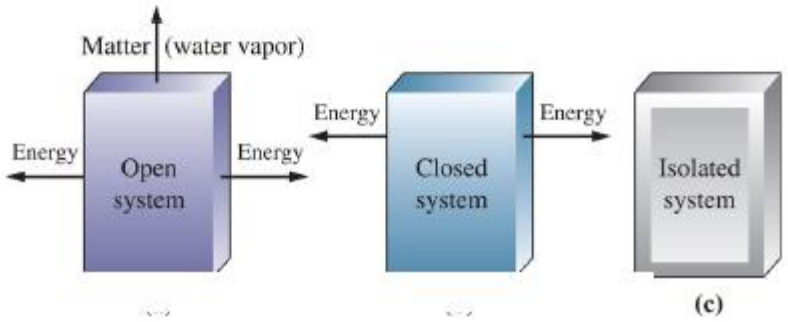
TERMOKİMYA



Evrenin incelenmek üzere seçilen bölümüne ***sistem*** adı verilir.
Sistem dışında kalan evren parçasına ***çevre*** adı verilir.

Kinetic Energy

$$e_k = \frac{1}{2} mv^2 \qquad [e_k] = \mathrm{kg}\left(\frac{\mathrm{m}}{\mathrm{s}}\right)^2 = \mathrm{J}$$

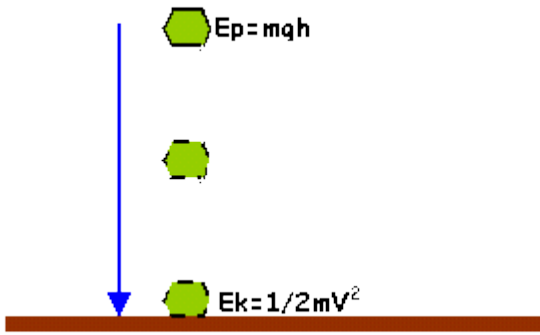
Potential Energy

$$E_p = k\frac{q_1 . q_2}{d}$$

Work

$$w = F \times d$$

$$= m \times a \times d \qquad [w] = \mathrm{kg}\left(\frac{\mathrm{m}}{\mathrm{s}^2}\right)\mathrm{m} = \mathrm{J}$$



Enerji iş yapabilme kapasitesidir. Bir kuvvetin bir yol boyunca etkimesi bir ***iş*** yapar.

Haraketli cismin enerjisine ***kinetik enerji*** denir.

Potansiyel enerji, cisimler arasındaki itme ya da çekme kuvvetlerinden veya konumundan ve bileşiminden ileri gelen bir enerji çeşididir.

Isı sıcaklık farkından ileri gelen enerji alışverişidir.
Sıcak bir cisimden soğuk bir cisme enerji aktarımı ısı şeklinde olur.

Units of Heat

Calorie (cal)

The quantity of heat required to change the temperature of one gram of water by one degree Celsius.

Joule (J)

SI unit for heat

$$1 \text{ cal} = 4.184 \text{ J}$$

Heat Capacity

The quantity of heat required to change the temperature of a system by one degree.

Molar heat capacity.
System is one mole of substance.

Specific heat capacity, c.
System is one gram of substance

$q = mc\Delta T$

Heat capacity
(Mass of system) x specific heat.

$q = C\Delta T$

maddenin kütlesi (g) x özgül ısı (**c**) = **C** (ısı kapasitesi)

Isı miktarı (q) = m x c x delta T = C x delta T

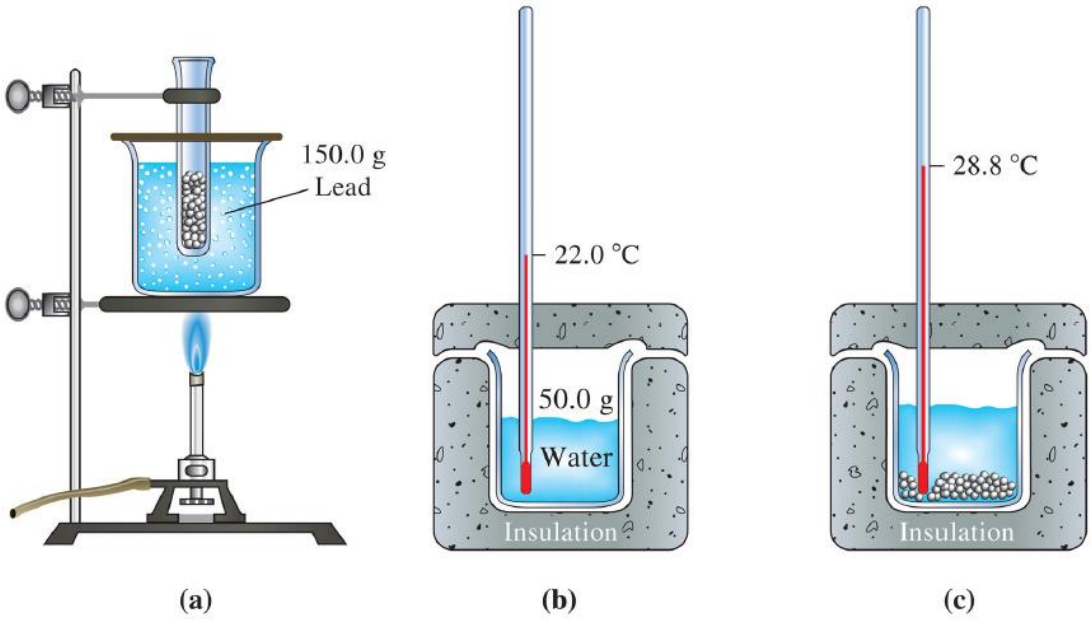
Specific heat capacity (c) = özgül ısı kapasitesi =özgül ısı

Law of conservation of energy

In interactions between a system and its surroundings the total energy remains *constant—energy is neither created nor destroyed.*

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

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



▲ FIGURE 7-3
Determining the specific heat of lead – Example 7-2 illustrated

Solve

First, use equation (7.5) to calculate q_{water}.

$$q_{water} = 50.0\,\text{g water} \times \frac{4.18\,\text{J}}{\text{g water °C}} \times (28.8 - 22.0)\,\text{°C} = 1.4 \times 10^3\,\text{J}$$

From equation (7.8) we can write

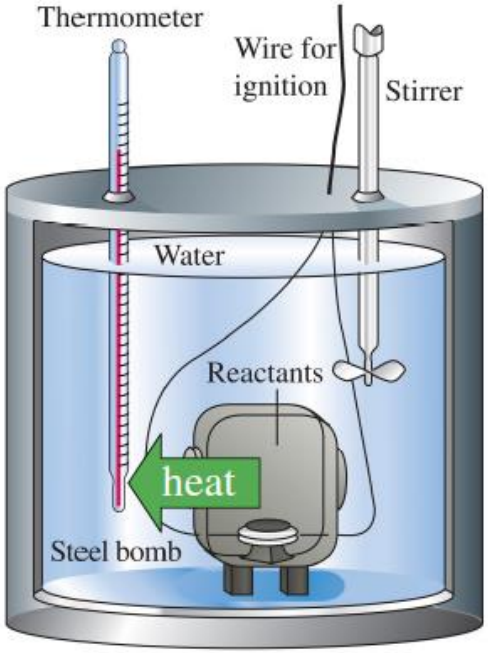
$$q_{lead} = -q_{water} = -1.4 \times 10^3\,\text{J}$$

Now, from equation (7.5) again, we obtain

$$q_{lead} = 150.0\,\text{g lead} \times \text{specific heat of lead} \times (28.8 - 100.0)\,\text{°C} = -1.4 \times 10^3\,\text{J}$$

$$\text{specific heat of lead} = \frac{-1.4 \times 10^3\,\text{J}}{150.0\,\text{g lead} \times (28.8 - 100.0)\,\text{°C}} = \frac{-1.4 \times 10^3\,\text{J}}{150.0\,\text{g lead} \times -71.2\,\text{°C}} = 0.13\,\text{J g}^{-1}\,\text{°C}^{-1}$$

Bomb Calorimetry



▲ FIGURE 7-5
A bomb calorimeter assembly

$$q_{rxn} = -q_{cal}$$

$$q_{cal} = q_{bomb} + q_{water} + q_{wires} + \ldots$$

Define the heat capacity of the calorimeter:

$$q_{cal} = \sum_{all\ i} m_i c_i \Delta T = C_{cal} \Delta T$$

Example 7-3

Using Bomb Calorimetry Data to Determine a Heat of Reaction.

The combustion of 1.010 g sucrose, in a bomb calorimeter, causes the temperature to rise from 24.92 to 28.33°C. The heat capacity of the calorimeter assembly is 4.90 kJ/°C.

(a) What is the heat of combustion of sucrose, expressed in kJ/mol $C_{12}H_{22}O_{11}$

(b) Verify the claim of sugar producers that one teaspoon of sugar (about 4.8 g) contains only 19 calories.

Example 7-3

Calculate $q_{calorimeter}$:

$$q_{cal} = C\Delta T = (4.90\ kJ/°C)(28.33\text{-}24.92)°C = (4.90)(3.41)\ kJ$$

$$= 17.7\ kJ$$

Calculate q_{rxn}:

$$q_{rxn} = -q_{cal} = -17.7\ kJ \quad \textit{per 1.010 g}$$

Example 7-3

Calculate q_{rxn} in the required units:

$$q_{rxn} = -q_{cal} = \frac{-17.7\ \text{kJ}}{1.010\ \text{g}} = -17.5\ \text{kJ/g}$$

$$q_{rxn} = -17.5\ \text{kJ/g}\ \frac{343.3\ \text{g}}{1.00\ \text{mol}}$$

$$= -5.75 \times 10^3\ \text{kJ/mol} \qquad \text{(a)}$$

Calculate q_{rxn} for one teaspoon:

$$q_{rxn} = (-17.5\ \text{kJ/g})\left(\frac{4.8\ \text{g}}{1\ \text{tsp}}\right)\left(\frac{1.00\ \text{cal}}{4.184\ \text{J}}\right) = -19\ \text{cal/tsp} \qquad \text{(b)}$$

The "Coffee-Cup" Calorimeter

A simple calorimeter.

Well insulated and therefore *isolated.*

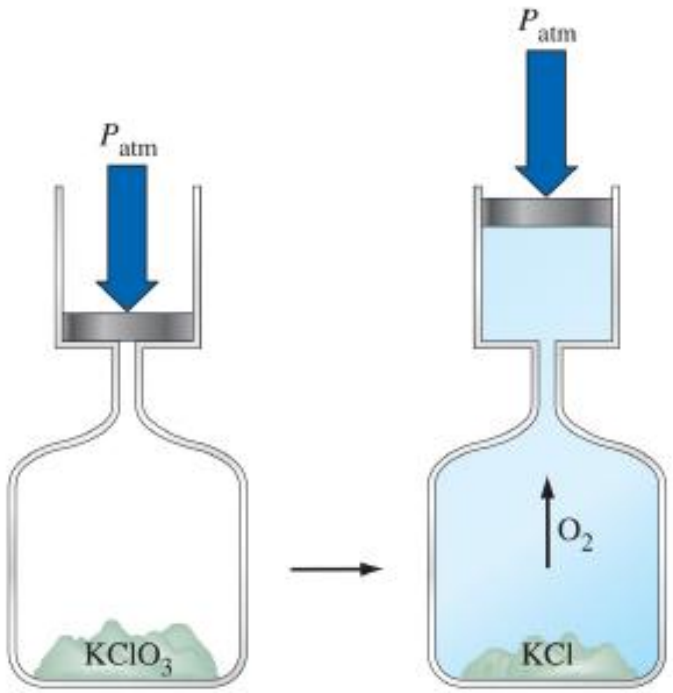
Measure temperature change.

$$q_{rxn} = -q_{cal}$$

▲ FIGURE 7-6

A Styrofoam "coffee-cup" calorimeter

7-4 Work



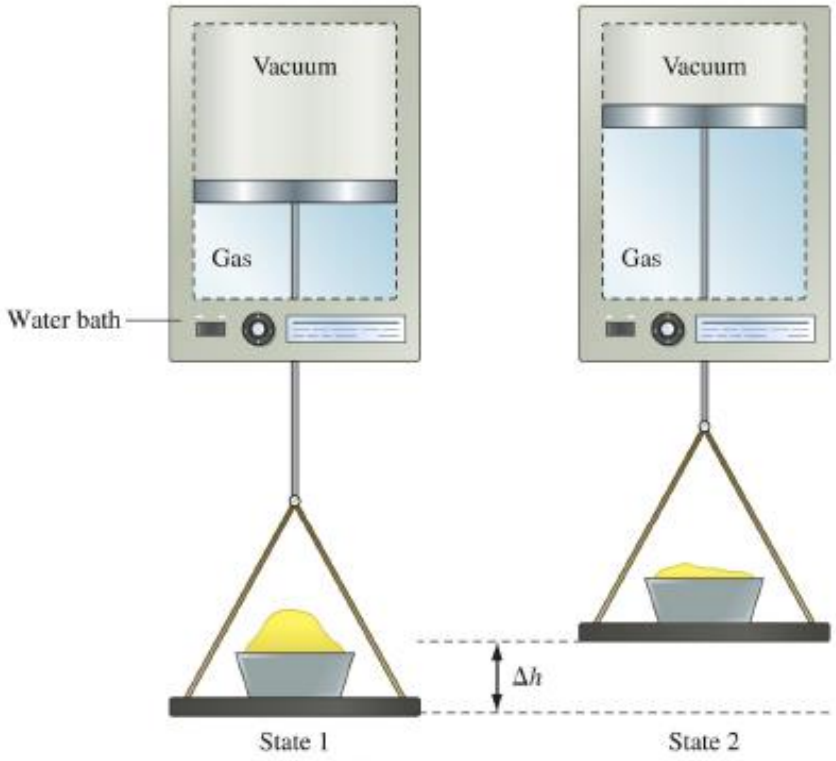
In addition to heat effects chemical reactions may also do *work*.

Gas formed pushes against the atmosphere.

The volume changes.

Pressure-volume work.

▲ FIGURE 7-7 **Illustrating work (expansion) during the chemical reaction** $2\ KClO_3(s) \longrightarrow 2\ KCl(s) + 3\ O_2(g)$

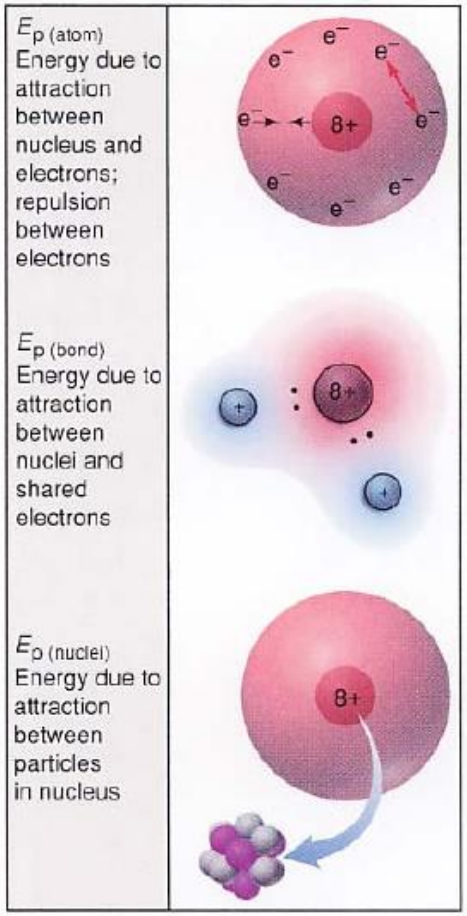


$$w = F \times d$$
$$= (m \times g) \times \Delta h$$
$$= \frac{(m \times g)}{A} \times \Delta h \times A$$
$$= P\Delta V$$
$$w = -P_{ext}\Delta V$$

▲ FIGURE 7-8
Pressure-volume work

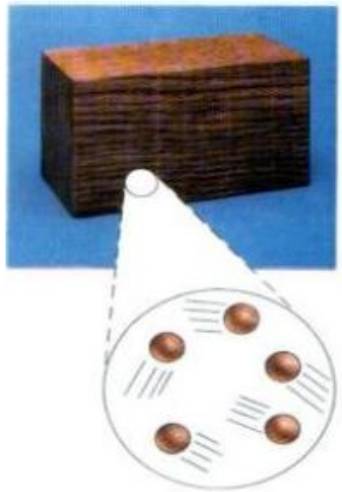
İÇ ENERJİ: Bir sistemin kinetik ve potansiyel enerjilerinin toplamıdır.

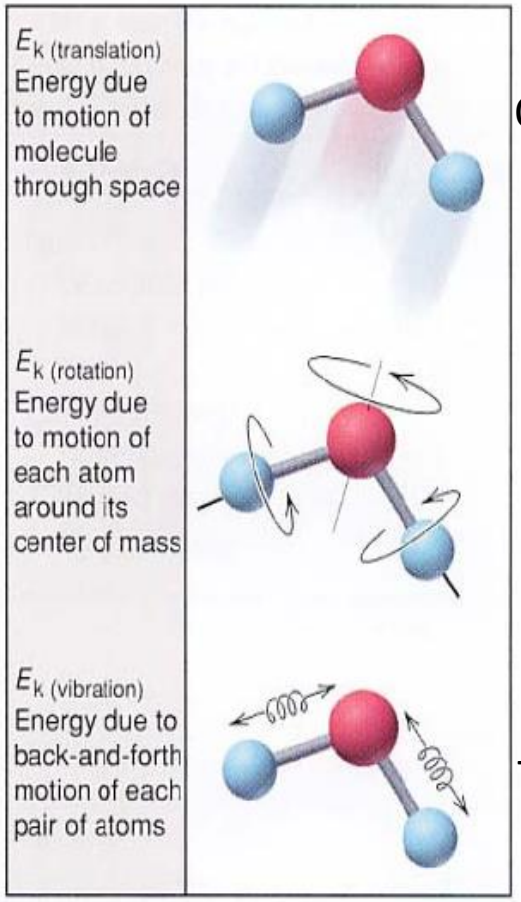
INTERNAL ENERGY



1. Electronic Energy
2. Rotational Energy
3. Vibrational Energy
4. Translational Energy

$$E = E_e + E_r + E_v + E_t$$





Öteleme E

Dönme E

Titreşim E

The First Law of Thermodynamics

A system contains *only* internal energy.

A system does not contain heat or work.

These only occur during a *change* in the system.

$$\Delta U = q + w$$

Law of Conservation of Energy

The energy of an isolated system is constant

Isı ve iş, sistemin çevresi ile enerji değişimlerindeki bir araçtır. $\Delta U_{\text{yalıtılmış sistem}} = 0$ dır.

Isı (q), iş (w) ve iç enerji değişimi (ΔU) arasındaki ilişki ***Termodinamiğin 1. yasası*** olarak bilinir.

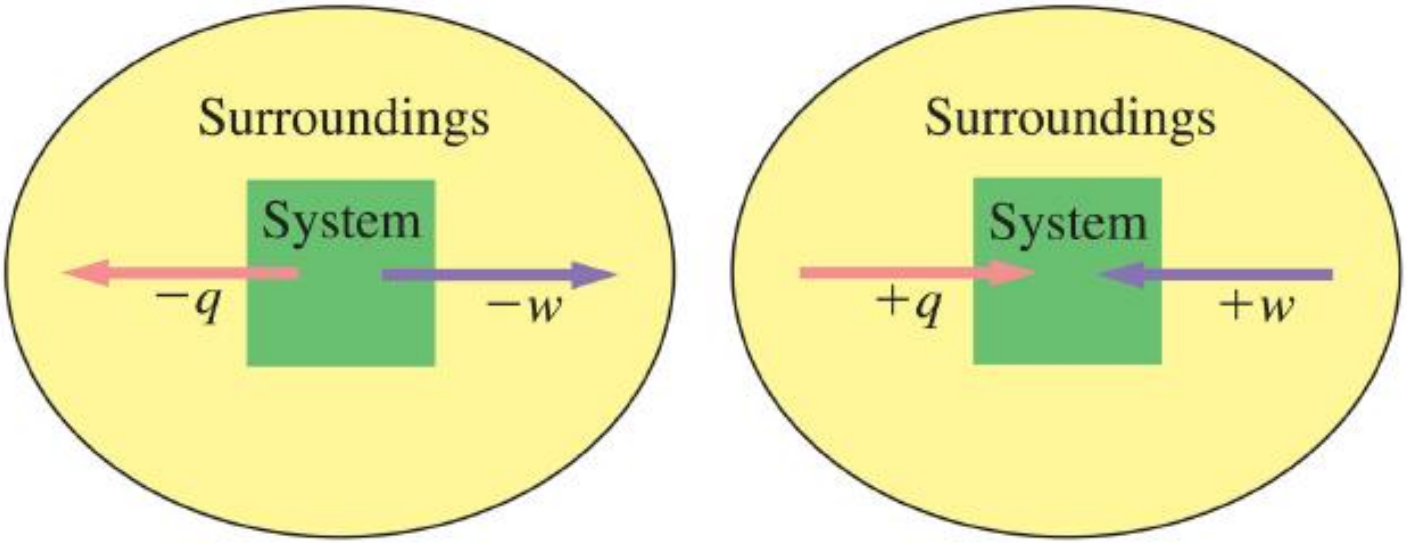
The First Law of Thermodynamics

An isolated system is unable to exchange either heat or work with its surroundings, so that $\Delta U_{isolated\ system} = 0$, and we can say:

The energy of an isolated system is constant.

Sistemden çıkan enerji **-** işaretlidir.

Sisteme giren enerji **+** işaretlidir.



▲ FIGURE 7-10
Illustration of sign conventions used in thermodynamics

7-6 Heats of Reaction: ΔU and ΔH

Reactants → Products

U_i U_f

$$\Delta U = U_f - U_i$$

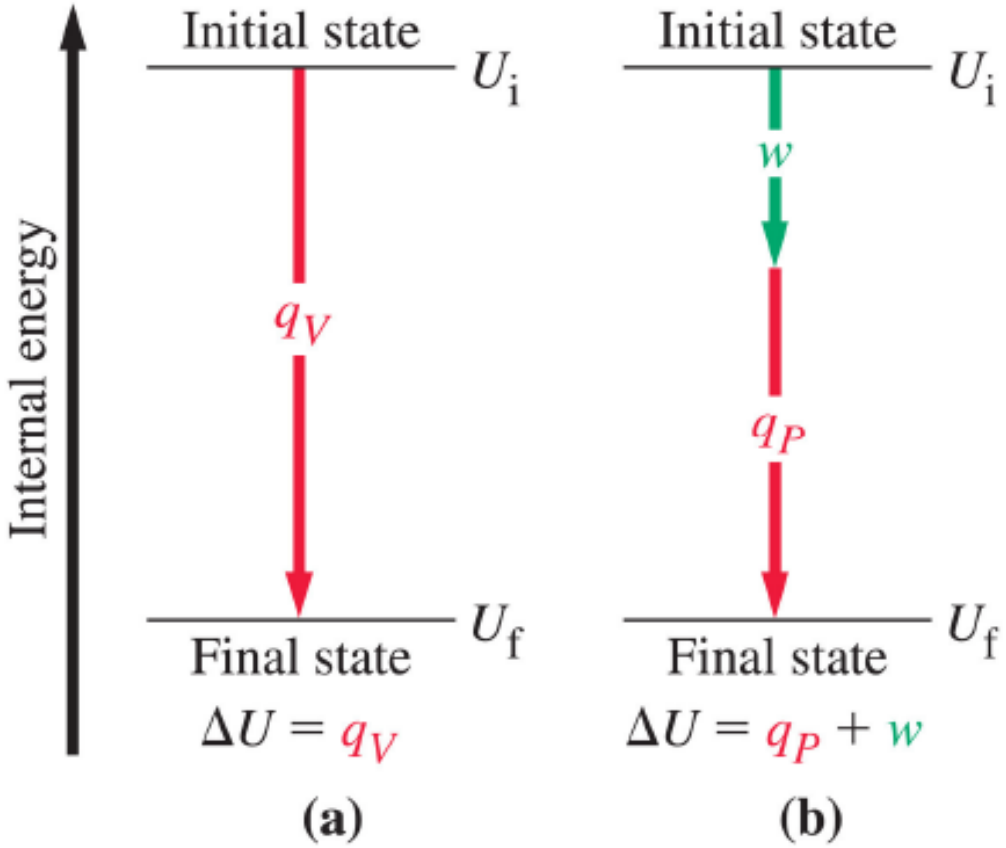
$$\Delta U = q_{rxn} + w$$

In a system at constant volume (bomb calorimeter):

$$\Delta U = q_{rxn} + 0 = q_{rxn} = q_v$$

But we live in a constant pressure world!

How does q_p relate to q_v?



▲ FIGURE 7-13

Two different paths leading to the same internal energy change in a system

Heats of Reaction

$$q_V = q_P + w$$

We know that $w = -P\Delta V$ and $\Delta U = q_v$, therefore:

$$\Delta U = q_P - P\Delta V$$

$$q_P = \Delta U + P\Delta V$$

These are all state functions, so define a new function.

Let **enthalpy** be $H = U + PV$

Then $\Delta H = H_f - H_i = \Delta U + \Delta PV$

If we work at constant pressure and temperature:

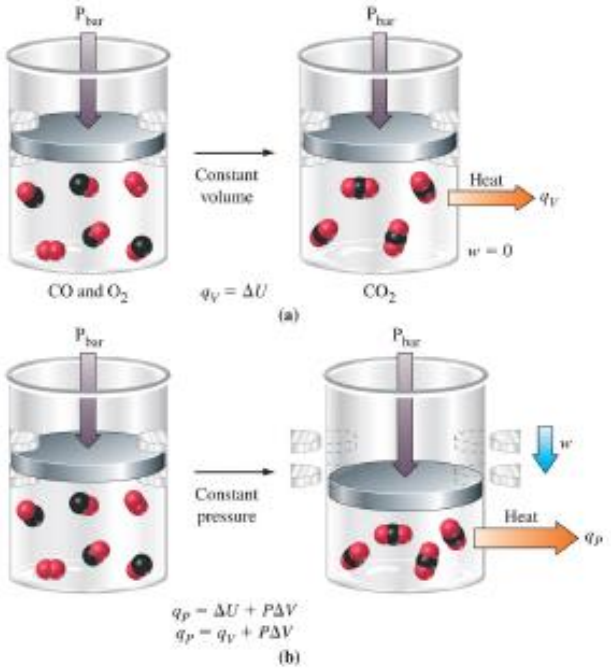
$$\Delta H = \Delta U + P\Delta V = q_P$$

Entalpi, H, hacim-basınç işi ile iç enerjinin toplamına eşittir.

Comparing Heats of Reaction

Sabit hacim:
İş yapılmıyor.

Sabit basınç:
Çevre sisteme iş yapar ve sistem daha küçük bir hacme sıkıştırılır. Sabit hacimdeki tepkimeye göre daha fazla ısı açığa çıkar.

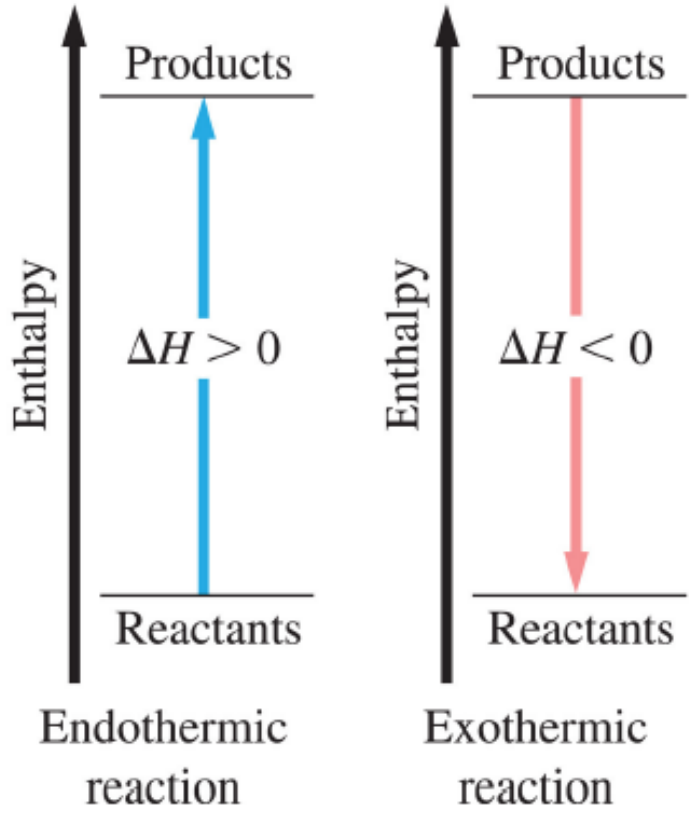


$$q_V = \Delta U = \Delta H - P\Delta V$$
$$= -563.5 \text{ kJ/mol}$$

$$w = P\Delta V = P(V_f - V_i)$$
$$= RT(n_f - n_i)$$
$$= -2.5 \text{ kJ}$$

$$q_P = \Delta H$$
$$= -566 \text{ kJ/mol}$$

▲ FIGURE 7-14
Comparing heats of reaction at constant volume and constant pressure for the reaction $2\ CO(g) + 2\ O_2(g) \longrightarrow 2\ CO_2(g)$



▲ FIGURE 7-15
Enthalpy Diagrams

Hal Değişimlerinde Entalpi Değişimi

Mol buharlaşma entalpisi:

$$H_2O\ (l) \rightarrow H_2O(g) \qquad \Delta H = 44.0\ \text{kJ at } 298\ \text{K}$$

Mol erime entalpisi:

$$H_2O\ (s) \rightarrow H_2O(l) \qquad \Delta H = 6.01\ \text{kJ at } 273.15\ \text{K}$$

Standard States and Standard Enthalpy Changes

Define a particular state as a standard state.

Standard enthalpy of reaction, ΔH°

The enthalpy change of a reaction in which all reactants and products are in their standard states.

Standard State

The pure element or compound at a pressure of 1 *bar* and at the temperature of interest.

Sıvı ya da katı bir maddenin standard hali, saf element ve bileşiklerde 1 bar (10^5 Pa) basınç ve çalışılan sıcaklıktaki halidir.

Gazların standard hali, 1 bar basınç ve çalışılan sıcaklıktaki ideal gaz gibi davrandığı halidir.

7-7 Indirect Determination of ΔH: Hess's Law

ΔH bir kapasite özelliğidir.

- ΔH is an extensive property.

  Enthalpy change is directly proportional to the amount of substance in a system.

$$N_2(g) + O_2(g) \rightarrow 2\ NO(g) \qquad \Delta H^\circ = +180.50\ kJ$$

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

Tepkime tersine döndüğünde ΔH ın işareti değişir.

- ΔH changes sign when a process is reversed

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

- Hess's law of constant heat summation

Hess'in tepkime ısılarının toplanabilirliği yasası

$$\tfrac{1}{2}N_2(g) + O_2(g) \rightarrow NO(g) + \tfrac{1}{2}O_2(g) \quad \Delta H^\circ = +90.25\ \text{kJ}$$

$$NO(g) + \tfrac{1}{2}O_2(g) \rightarrow NO_2(g) \quad \Delta H^\circ = -57.07\ \text{kJ}$$

$$\tfrac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g) \quad \Delta H^\circ = +33.18\ \text{kJ}$$

If a process occurs in stages or steps (even hypothetically), the enthalpy change for the overall process is the sum of the enthalpy changes for the individual steps.

Standard Oluşum Entalpisi

7-8 Standard Enthalpies of Formation ΔH_f°

The enthalpy change that occurs in the formation of one mole of a substance in the standard state from the reference forms of the elements in their standard states.

The standard enthalpy of formation of a pure element in its reference state is 0.

TABLE 7.2 Some Standard Molar Enthalpies of Formation, ΔH_f° at 298.15 K

Substance	kJ/mol[a]	Substance	kJ/mol[a]
$CO(g)$	−110.5	$HBr(g)$	−36.40
$CO_2(g)$	−393.5	$HI(g)$	26.48
$CH_4(g)$	−74.81	$H_2O(g)$	−241.8
$C_2H_2(g)$	226.7	$H_2O(l)$	−285.8
$C_2H_4(g)$	52.26	$H_2S(g)$	−20.63
$C_2H_6(g)$	−84.68	$NH_3(g)$	−46.11
$C_3H_8(g)$	−103.8	$NO(g)$	90.25
$C_4H_{10}(g)$	−125.6	$N_2O(g)$	82.05
$CH_3OH(l)$	−238.7	$NO_2(g)$	33.18
$C_2H_5OH(l)$	−277.7	$N_2O_4(g)$	9.16
$HF(g)$	−271.1	$SO_2(g)$	−296.8
$HCl(g)$	−92.31	$SO_3(g)$	−395.7

[a]Values are for reactions in which one mole of substance is formed. Most of the data have been rounded off to four significant figures.

Standard tepkime entalpilerinden tepkime ısısının hesaplanması:

$$\Delta H^\circ = \sum \nu_p \Delta H_f^\circ(\text{products}) - \sum \nu_r \Delta H_f^\circ(\text{reactants}) \quad (7.21)$$

Ionic Reactions in Solutions

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad \Delta H^\circ = -55.8\ \text{kJ} \tag{7.22}$$

$$\Delta H^\circ = 1\ \text{mol}\ H_2O \times \Delta H_f^\circ[H_2O(l)] - \{1\ \text{mol}\ H^+ \times \Delta H_f^\circ[H^+(aq)] + 1\ \text{mol}\ OH^- \times \Delta H_f^\circ[OH^-(aq)]\} = -55.8\ \text{kJ}$$

$$\Delta H_f^\circ[OH^-(aq)] = \frac{55.8\ \text{kJ} + (1\ \text{mol}\ H_2O \times \Delta H_f^\circ[H_2O(l)]) - (1\ \text{mol}\ H^+ \times \Delta H_f^\circ[H^+(aq)])}{1\ \text{mol}\ OH^-}$$

$$\Delta H_f^\circ[OH^-(aq)] = \frac{55.8\ \text{kJ} - 285.8\ \text{kJ} - 0\ \text{kJ}}{1\ \text{mol}\ OH^-} = -230.0\ \text{kJ/mol}\ OH^-$$

TABLE 7.3 Some Standard Molar Enthalpies of Formation, ΔH_f° of Ions in Aqueous Solution at 298.15 K

Ion	kJ/mol	Ion	kJ/mol
H^+	0	OH^-	−230.0
Li^+	−278.5	Cl^-	−167.2
Na^+	−240.1	Br^-	−121.6
K^+	−252.4	I^-	−55.19
NH_4^+	−132.5	NO_3^-	−205.0
Ag^+	105.6	CO_3^{2-}	−677.1
Mg^{2+}	−466.9	S^{2-}	33.05
Ca^{2+}	−542.8	SO_4^{2-}	−909.3
Ba^{2+}	−537.6	$S_2O_3^{2-}$	−648.5
Cu^{2+}	64.77	PO_4^{3-}	−1277
Al^{3+}	−531		