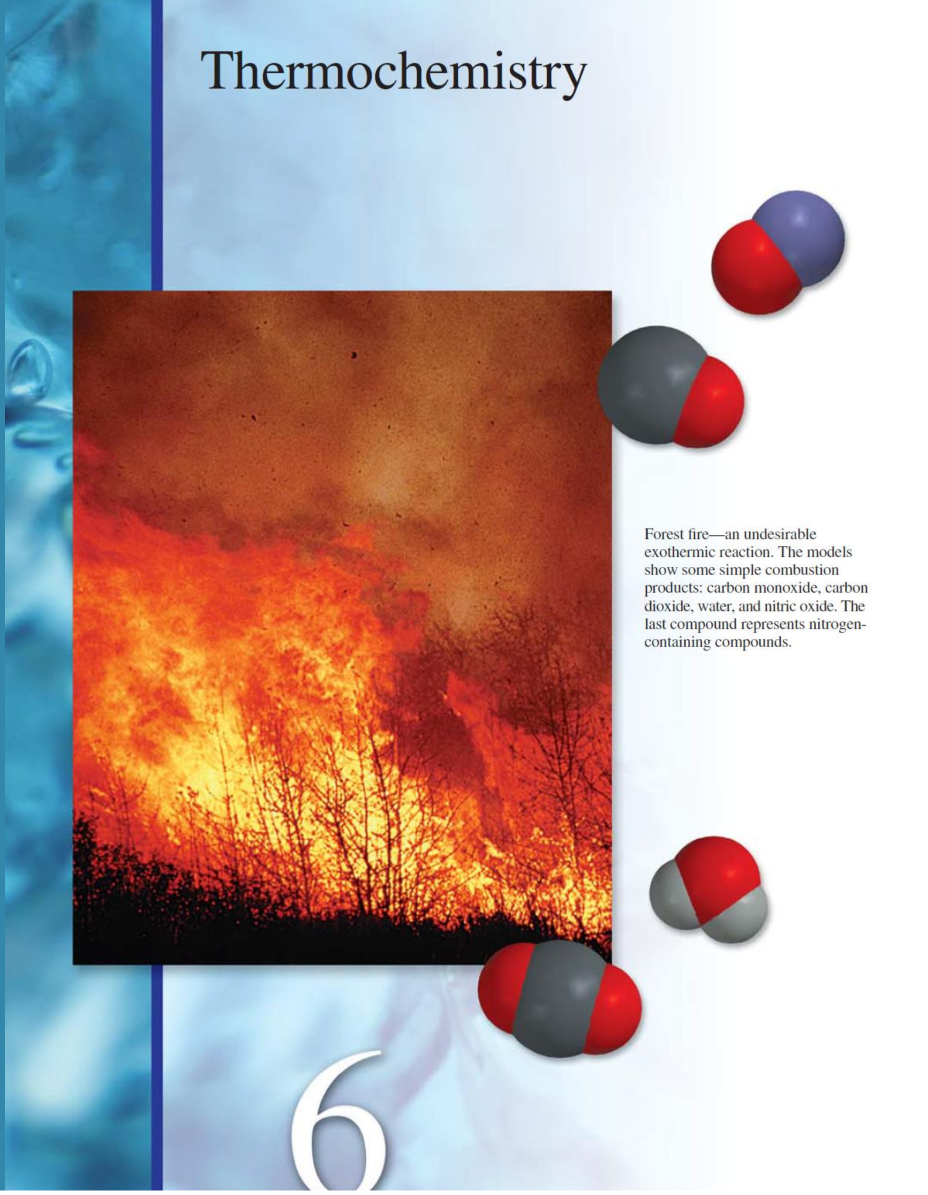
Thermochemistry

Chapter 6

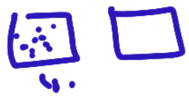
Chapter Outline

- **The Nature of Energy and Types of Energy.**
- **Introduction to Thermodynamics.**
- **Enthalpy of Chemical Reactions.**
- **Calorimetry.**
- **Standard Enthalpy of Formation and Reaction.**
- **Heat of Solution and Dilution.**



Energy is the capacity to do work.

- ***Radiant energy*** comes from the sun and is earth's primary energy source



- ***Thermal energy*** is the energy associated with the random motion of atoms and molecules
- ***Chemical energy*** is the energy stored within the bonds of chemical substances
- ***Nuclear energy*** is the energy stored within the collection of neutrons and protons in the atom
- ***Potential energy*** is the energy available by virtue of an object's position

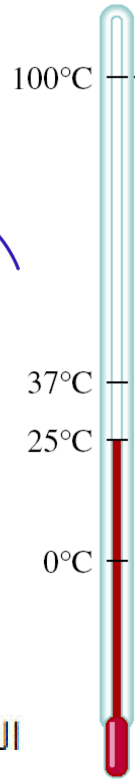
الطاقة هي القدرة على إنجاز عمل.

- **الطاقة الإشعاعية** تأتي من الشمس وهي المصدر الرئيسي للطاقة على الأرض.
- **الطاقة الحرارية** هي الطاقة المرتبطة بالحركة العشوائية للذرات والجزيئات.
- **الطاقة الكيميائية** هي الطاقة المخزنة داخل الروابط بين المواد الكيميائية.
- **الطاقة النووية** هي الطاقة المخزنة داخل تجمع النيوترونات والبروتونات في الذرة.
- **الطاقة الكامنة** هي الطاقة المتاحة بفضل موضع الجسم.

Energy Changes in Chemical Reactions

Heat is the transfer of **thermal energy** between two bodies that are at different temperatures.

Temperature is a measure of the **thermal energy**.



Temperature = Thermal Energy

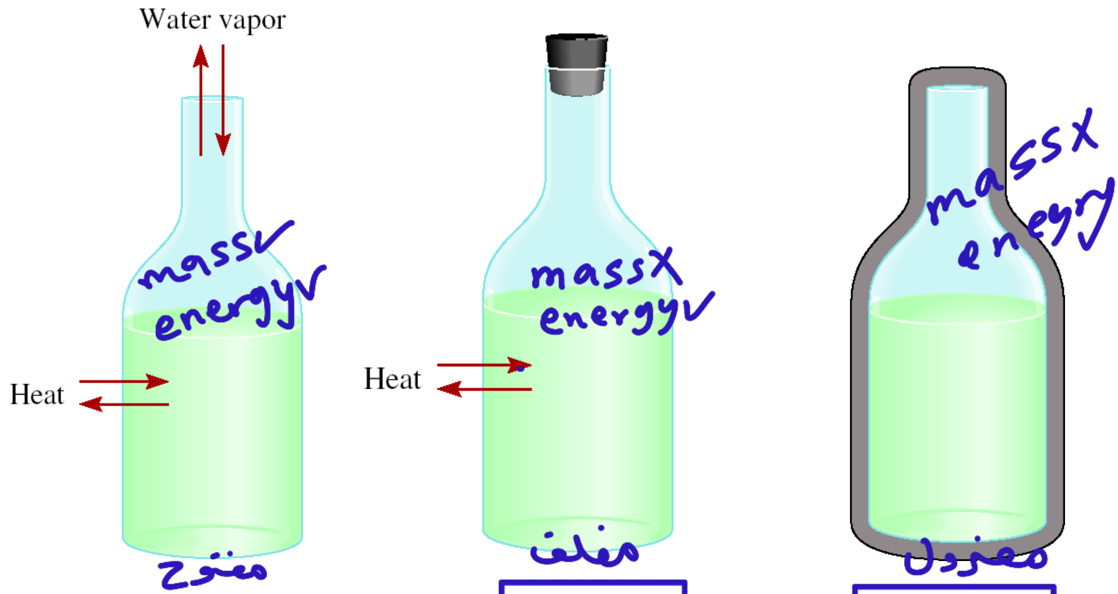
الحرارة هي انتقال الطاقة الحرارية بين جسمين يختلفان في درجة الحرارة.

درجة الحرارة هي مقياس للطاقة الحرارية.

درجة الحرارة = الطاقة الحرارية.

Thermochemistry is the study of heat change in chemical reactions.

The ***system*** is the specific part of the universe that is of interest in the study.



	open	closed	isolated
Exchange: (تبادل)	mass & energy	energy	nothing
	يسمح بتبادل الطاقة والكتلة	يسمح بتبادل الطاقة فقط	لا يسمح بتبادل الطاقة او الكتلة

الكيمياء الحرارية هي دراسة تغير الحرارة في التفاعلات الكيميائية.

النظام هو الجزء المحدد من الكون الذي يتم التركيز عليه في الدراسة.

العملية الطاردة للحرارة هي أي عملية تطلق حرارة، حيث تنتقل الطاقة الحرارية من النظام إلى المحيط.

Exothermic process is any process that gives off heat – transfers thermal energy from the system to the surroundings.

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (l) + \text{energy}$$

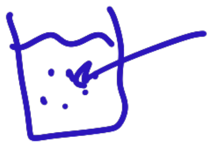
$$H_2O\ (g) \longrightarrow H_2O\ (l) + \text{energy}$$

العملية الماصة للحرارة هي أي عملية تحتاج إلى تزويد النظام بالحرارة من المحيط.

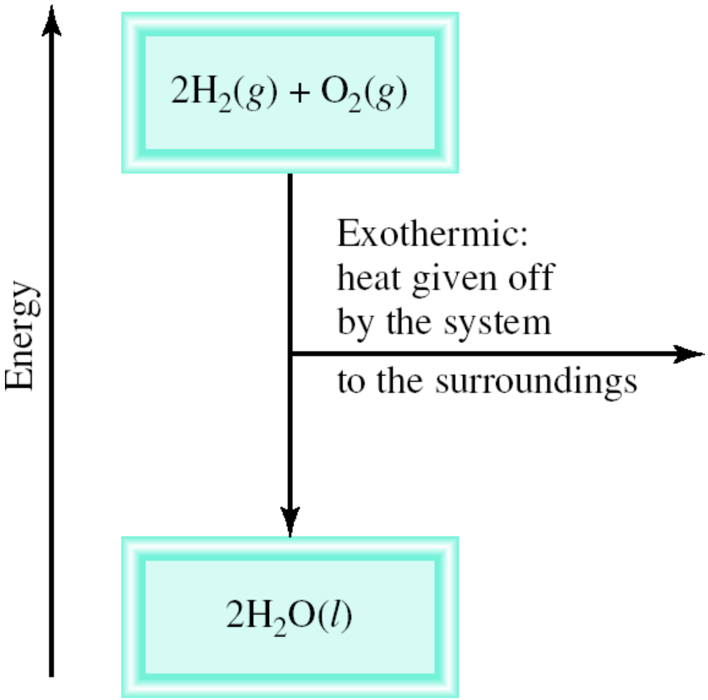
Endothermic process is any process in which heat has to be supplied to the system from the surroundings.

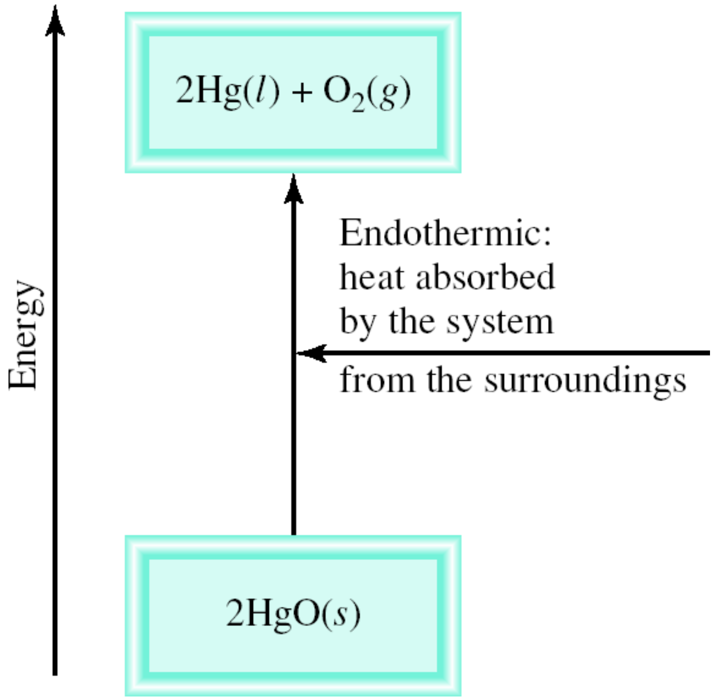
$$\text{energy} + 2HgO\ (s) \longrightarrow 2Hg\ (l) + O_2\ (g)$$

$$\text{energy} + H_2O\ (s) \longrightarrow H_2O\ (l)$$



Schematic of Exothermic and Endothermic Processes

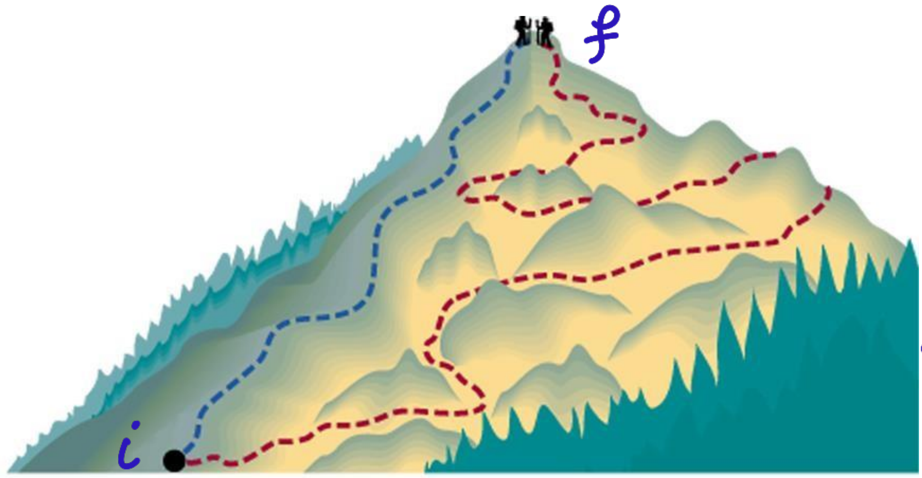




Thermodynamics is the scientific study of the interconversion of heat and other kinds of energy.

State functions are properties that are determined by the state of the system, regardless of how that condition was achieved.

energy, pressure, volume, temperature



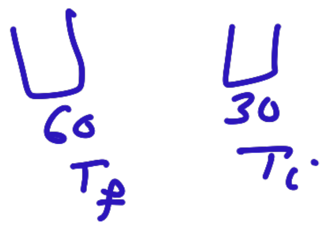
طاقة $\Delta E = E_{final} - E_{initial}$

ضغط $\Delta P = P_{final} - P_{initial}$

حجم $\Delta V = V_{final} - V_{initial}$

درجة $\Delta T = T_{final} - T_{initial}$

Potential energy of hiker 1 and hiker 2 is the same even though they took different paths.



الديناميكا الحرارية هي الدراسة العلمية لتحويل الحرارة وأشكال الطاقة الأخرى.

دوال الحالة هي خصائص تُحدد بناءً على حالة النظام، بغض النظر عن الطريقة التي تم بها الوصول إلى تلك الحالة.

أمثلة على دوال الحالة: الطاقة، الضغط، الحجم، ودرجة الحرارة.

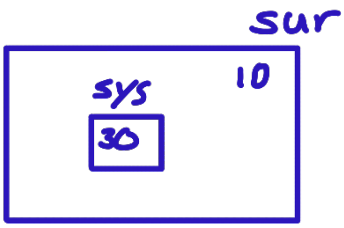
First law of thermodynamics – energy can be converted from one form to another, but cannot be created or destroyed. القانون الأول للديناميكا الحرارية: يمكن تحويل الطاقة من شكل إلى آخر، لكنها لا تُخلق ولا تُفنى.

$$\Delta E_{system} + \Delta E_{surroundings} = 0$$

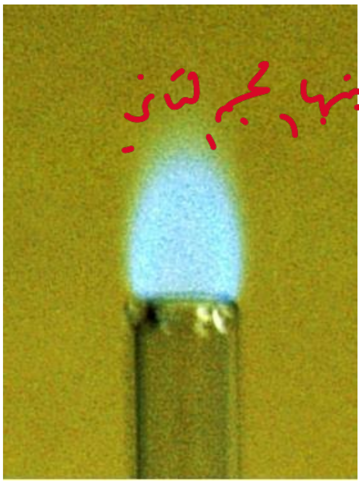
$(20 - 30 = -10) \quad (20 - 10 = 10)$

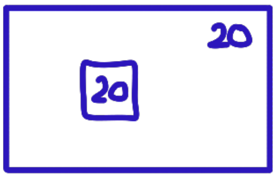
or

$$\Delta E_{system} = -\Delta E_{surroundings}$$



الطاقة المفقودة من الجسم الأول = الطاقة التي اكتسبها الجسم الثاني





$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

Exothermic chemical reaction!

تفاعل احتراق طارد للطاقة

Chemical energy **lost** (مفقود) by combustion = Energy **gained** (مكتسب) by the surroundings

system surroundings

الطاقة الكيميائية المفقودة نتيجة الاحتراق = الطاقة المكتسبة من قبل المحيط.

Another form of the ***first law*** for ΔE_{system}

$\Delta E = q + w$

ΔE is the change in internal energy of a system

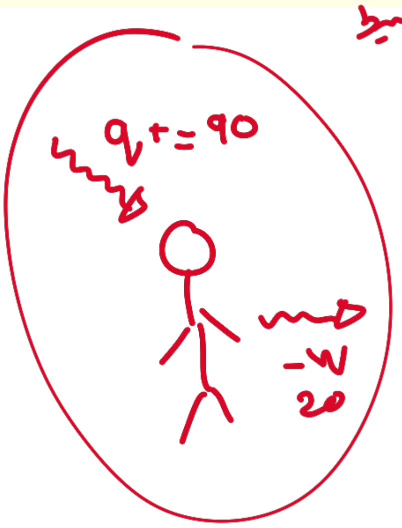
q is the heat exchange between the system and the surroundings

w is the work done on (or by) the system

$w = -P\Delta V$ when a gas expands against a constant external pressure

TABLE 6.1 Sign Conventions for Work and Heat

Process	**Sign**
Work done by the system on the surroundings	−
Work done on the system by the surroundings	+
Heat absorbed by the system from the surroundings (endothermic process)	+
Heat absorbed by the surroundings from the system (exothermic process)	−



$\Delta E = 90 - 20$

$= 70$

صيغة أخرى للقانون الأول للديناميكا الحرارية للنظام:

$$w + q = \Delta E$$

حيث:

- ΔE: التغير في الطاقة الداخلية للنظام.
- q: التبادل الحراري بين النظام والمحيط.
- w: الشغل المبذول على (أو بواسطة) النظام.

عندما يتمدد الغاز ضد ضغط خارجي ثابت:

$$P\Delta V - = w$$

حيث:

- P: الضغط الخارجي الثابت.
- ΔV: التغير في حجم الغاز.

$W = -P\Delta V$

Work Done On the System

$W = F \times d$

$= P \times d^2 \times d$

$= P d^3$

$W = PV$

$d^2 =$ المساحة

$d^3 =$ الحجم

$w = F \times d$

$w = -P \Delta V$

$P \times V = \frac{F}{d^2} \times d^3 = F \times d = w$

(P: ضغط ، V: حجم)

زيادة حجم $\Delta V > 0$

الشغل سالب $-P\Delta V < 0$

الشغل الكلي سالب $w_{sys} < 0$

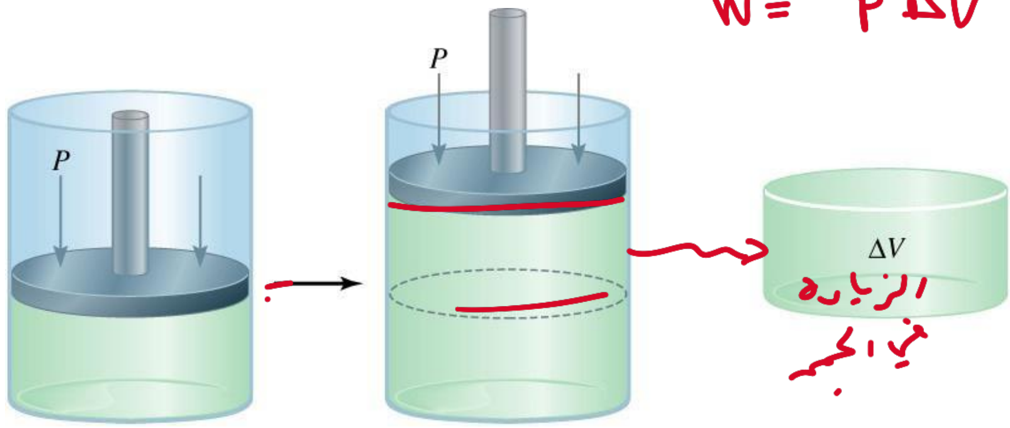
إذا كان الحجم متغير والضغط ثابت

$W = -P\Delta V$

Work is not a state function.

$\Delta w \neq w_{final} - w_{initial}$

الشغل يعتمد على طريقة
الحدوث وليس فقط
على نقطة النهاية والبداية



initial final

A sample of nitrogen gas expands in volume from 1.6 L to 5.4 L at constant temperature. What is the work done in joules if the gas expands (a) against a vacuum and (b) against a constant pressure of 3.7 atm?

ضغط = صفر

V_i 1.6 V_f 5.4

$\Delta V = 5.4 - 1.6 = 3.8$

$$w = -P\,\Delta V$$

(a) $\Delta V = 5.4\text{ L} - 1.6\text{ L} = 3.8\text{ L}$ $P = 0\text{ atm}$

$W = -0\text{ atm} \times 3.8\text{ L} = 0\text{ L•atm} = 0\text{ joules}$

(b) $\Delta V = 5.4\text{ L} - 1.6\text{ L} = 3.8\text{ L}$ $P = 3.7\text{ atm}$

$w = -3.7\text{ atm} \times 3.8\text{ L} = -14.1\text{ L•atm}$

$$w = -14.1\text{ L•atm} \times \frac{101.3\text{ J}}{1\text{ L•atm}} = -1430\text{ J}$$

(a) $W = -P\Delta V$
$W = -(0)(3.8)$
$= \text{zero J}$

(b) $W = -P\Delta V$
$= -(3.7)(3.8)$
$= -3.7 \times 1.013 \times 10^5 \times \frac{3.8}{1000}$
$= -1430$

لحساب الشغل والطاقة بوحدة جول يجب ان
تكون الضغط بوحدة باسكال والحجم بوحدة m^3

Pa → atm: ÷ 1.013×10^5; atm → Pa: × 1.013×10^5

m^3 → L: × 1000; L → m^3: ÷ 1000

L·atm → J: × 101.3; J → L·atm: ÷ 101.3

Chemistry in Action: Making Snow

$W = -P\Delta V$ تمدد

$W = P\Delta V$ انضغاط

$\Delta E = q + w$

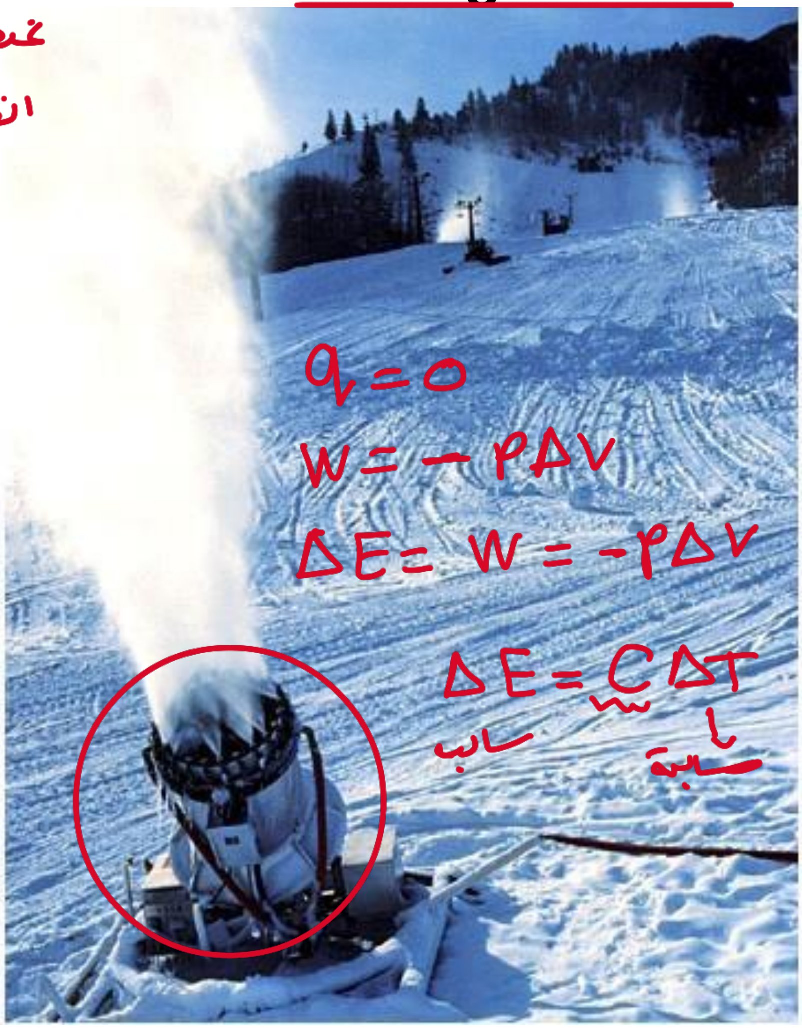
$q = 0$

سالب $w < 0$, $\Delta E < 0$ سالب

سالب $\Delta E = C\Delta T$ سالب

$\Delta T < 0$, SNOW!

سالبه جليد



Enthalpy and the First Law of Thermodynamics

$$\Delta E = q + w$$

At constant pressure:

$$q = \Delta H \text{ and } w = -P\Delta V$$

$$\Delta E = \Delta H - P\Delta V$$

$$\Delta H = \Delta E + P\Delta V$$

$\Delta H \approx q$

الطاقة الحرارية الممتصة او المفقودة

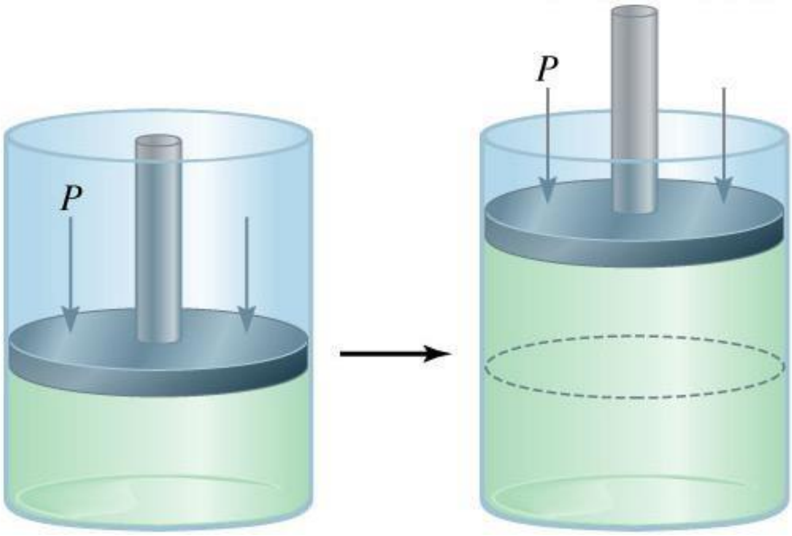
$q = \Delta H$

في حالة ثبوت الضغط

$\Delta E = \Delta H + W$

$\Delta E = \Delta H - P\Delta V$

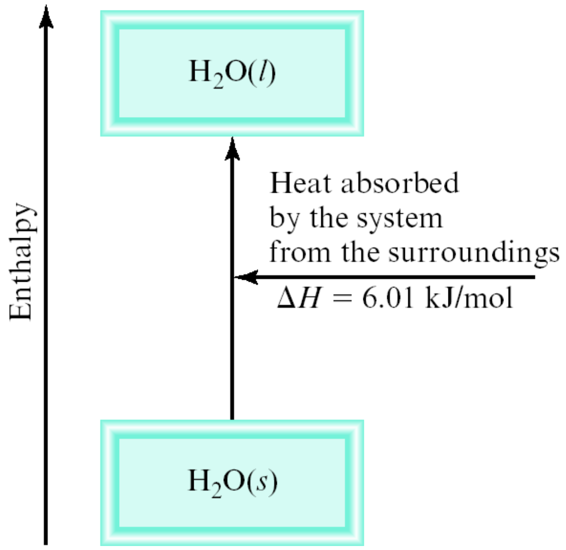
$\boxed{\Delta H = \Delta E + P\Delta V}$

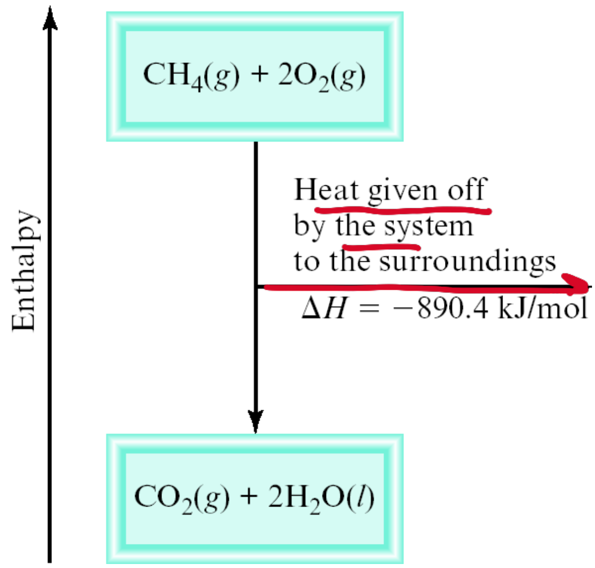


Enthalpy (H) is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

$$\Delta H = H\ (\text{products}) - H\ (\text{reactants})$$

ΔH = heat given off or absorbed during a reaction **at constant pressure**





$H_{\text{products}} > H_{\text{reactants}}$

$\Delta H > 0$

Endothermic

ΔH موجب

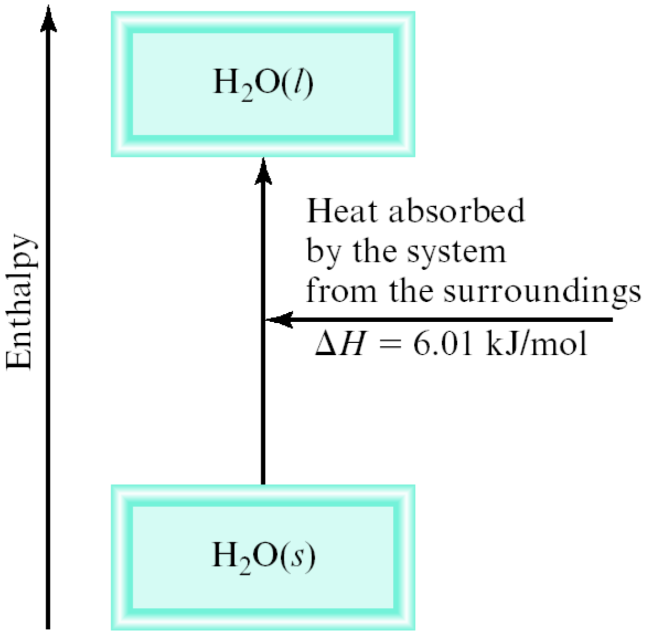
$H_{\text{products}} < H_{\text{reactants}}$

$\Delta H < 0$

ΔH = سالب

Exothermic

Thermochemical Equations



Is ΔH negative or positive?

System absorbs heat

Endothermic

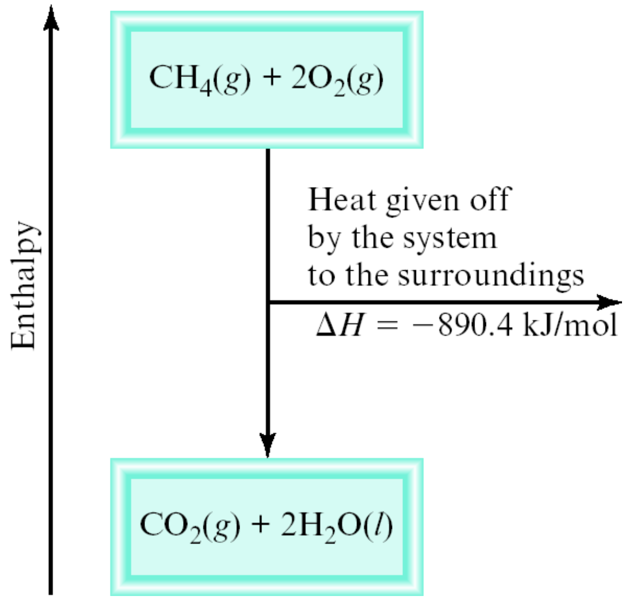
$\Delta H > 0$

6.01 kJ are absorbed for every 1 mole of ice that melts at 0^0C and 1 atm.

$$H_2O\ (s) \longrightarrow H_2O\ (l) \qquad \Delta H = 6.01 \text{ kJ/mol}$$

كمية الطاقة اللازمة لتحويل 1 مول
من الجليد الى ماء

Thermochemical Equations



Is ΔH negative or positive?

System gives off heat

Exothermic

$\Delta H < 0$

890.4 kJ are released for every 1 mole of methane that is combusted at 25⁰C and 1 atm.

$$CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(l) \quad \Delta H = -890.4 \text{ kJ/mol}$$

كمية الطاقة الناتجة من احتراق
1مول من CH4 مع 2O2

Thermochemical Equations

- The stoichiometric coefficients always refer to the number of moles of a substance

$$H_2O\ (s) \longrightarrow H_2O\ (l) \qquad \Delta H = 6.01\ \text{kJ/mol}$$

- If you reverse a reaction, the sign of ΔH changes

$$H_2O\ (l) \longrightarrow H_2O\ (s) \qquad \Delta H = -6.01\ \text{kJ/mol}$$

- If you multiply both sides of the equation by a factor n, then ΔH must change by the same factor n.

$$2H_2O\ (s) \longrightarrow 2H_2O\ (l) \qquad \Delta H = 2 \times 6.01 = 12.0\ \text{kJ}$$

* في حال عكس المعادلة (بيحول التفاعل من طارد الى ماص والعكس)
وتنعكس اشارة ΔH

* في حاله ضرب المعادله بقيمه ثابته n فان
قيمه ΔH ايضا تضرب بـ n

Given:

$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)\ \Delta H° = -92\ kJ$

Find:

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

Solution:

Since the reaction is reversed, the sign of ΔH° changes:

$\Delta H° = +92\ kJ$

$H_2O(l) \rightarrow H_2O(g)\ \Delta H° = 44\ kJ$

Find:

$3\ H_2O(l) \rightarrow 3\ H_2O(g)$

Solution:

Since the reaction is multiplied by 3, ΔH° is also multiplied by 3:

$\Delta H° = (3 \times 44) = 132\ kJ$

$A + B \rightarrow \cancel{C + D}\quad \Delta H_1$

$\cancel{C + D} \rightarrow E + F\quad \Delta H_2$

$A + B \rightarrow E + F\quad \Delta H_1 + \Delta H_2$

Given:

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)\ \Delta H° = -484\ kJ$

Find:

$4\ H_2O(g) \rightarrow 4\ H_2(g) + 2\ O_2(g)$

Solution:

- The reaction is **reversed**, so change the sign of ΔH°.
- The reaction is **multiplied by 2**, so multiply ΔH° by 2.

  $\Delta H° = (2 \times +484) = +968\ kJ$

Thermochemical Equations

- The physical states of all reactants and products must be specified in thermochemical equations.

$$H_2O(s) \longrightarrow H_2O(l) \quad \Delta H = 6.01 \text{ kJ/mol}$$

$$H_2O(l) \longrightarrow H_2O(g) \quad \Delta H = 44.0 \text{ kJ/mol}$$

How much heat is evolved when 266 g of white phosphorus (P_4) burn in air?

امول

$$P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s) \quad \Delta H = -3013 \text{ kJ/mol}$$

$$266 \text{ g } P_4 \times \frac{1 \text{ mol } P_4}{123.9 \text{ g } P_4} \times \frac{3013 \text{ kJ}}{1 \text{ mol } P_4} = 6470 \text{ kJ}$$

mass → عدد مولات → طاقة

kg → n → × 3013

$$n = \frac{m}{M_m} = \frac{266}{30.9 \times 4} = 2.15 \text{ mol}$$

$$\Delta H = 2.15 \times 3013 = 6477 \text{ kJ}$$

$$\Delta E = \Delta H - P\Delta V$$

A Comparison of ΔH and ΔE

$2Na\,(s) + 2H_2O\,(l) \longrightarrow 2NaOH\,(aq) + H_2\,(g)$ $\Delta H = -367.5$ kJ/mol

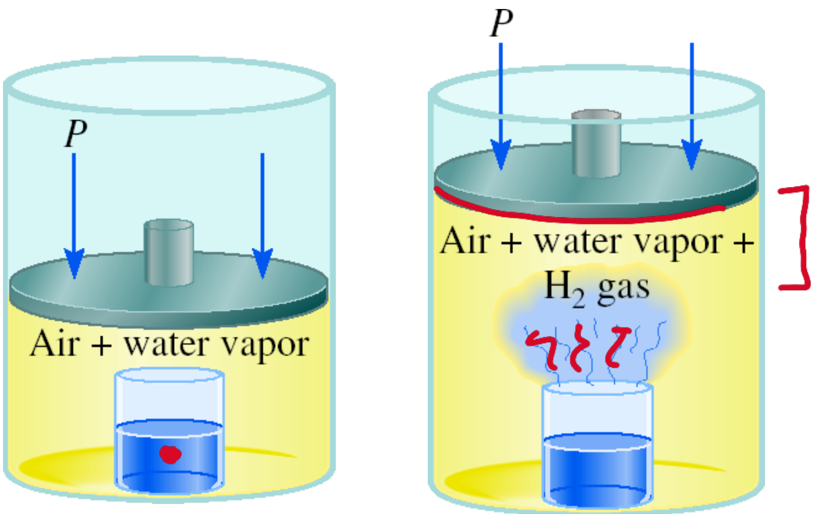
$\Delta E = \Delta H - P\Delta V$ At 25 °C, 1 mole H_2 = 24.5 L at 1 atm

$P\Delta V$ = 1 atm x 24.5 L = 2.5 kJ

$P = 1\ atm \times 1.013\times10^5\ Pa$

$\Delta V = 24.5\times10^{-3}$

ΔE = -367.5 kJ/mol – 2.5 kJ/mol = -370.0 kJ/mol



عند ثبوت الضغط يزداد الحجم

زيادة الحجم ناتجة عن تصاعد ١ مول من H_2

جميع الغازات لها نفس الحجم الأولي $V = 24.5 L$

$\Delta V = 24.5\ L$

$\Delta E = \Delta H - P\Delta V$

$\Delta E = -367.5 - 1.013\times10^5 \times 24.5\times10^{-3}\times10^{-3}$

$= -369.9$

≈ -370 KJ

الحرارة النوعية

The ***specific heat*** (**s**) of a substance is the amount of heat (*q*) required to raise the temperature of **one gram** of the substance by **one degree** Celsius.

السعة الحرارية

The ***heat capacity*** (**C**) of a substance is the amount of heat (*q*) required to raise the temperature of **a given quantity** (*m*) of the substance by **one degree** Celsius.

TABLE 6.2
The Specific Heats of Some Common Substances

Substance	Specific Heat (J/g · °C)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H_2O	4.184
C_2H_5OH (ethanol)	2.46

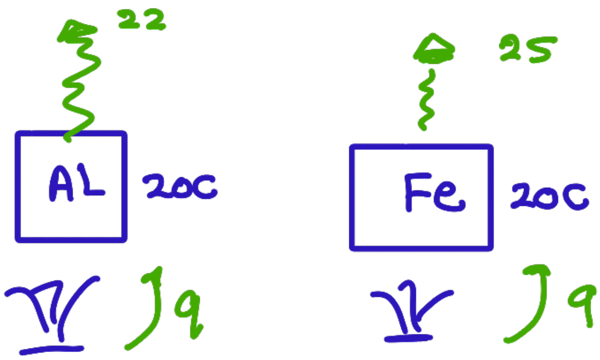
$$C = m \times s$$

Heat (*q*) absorbed or released:

$$q = m \times s \times \Delta t$$

$$q = C \times \Delta t$$

$$\Delta t = t_{final} - t_{initial}$$



S (الحرارة النوعية) : كمية الطاقة (q) اللازمة لرفع درجة حرارة
(1g) من المادة درجة سيلسيوس واحدة

J/g.C

وكلما كانت قيمة S اكبر تعني ان المادة تسخن ابطئ
وكلما كانت قيمة S اقل تعني ان المادة تسخن اسرع

الماء يعتبر اكثر المواد حرارة نوعية يعني او اكثر مادة تحتاج طاقة حتى تسخن او تبرد (يسخن ويبرد بشكل بطيء)

$$q = m \times S \times \Delta t$$

ما مقدار الطاقة اللازمة لرفع حرارة 3g من الحديد من درجة 10C° الى 15 °

$$q = m \times S \times \Delta t$$
$$= 3 \times 0.444 \times 5$$
$$= 6.66 J$$

(C) السعة الحرارية :- كمية الطاقة اللازمة لرفع حرارة كمية من المادة درجة سيليزية واحدة

$$C = J/C$$

$$q = C \times \Delta t$$

$$C = S \times m$$

q

How much heat is given off when an 869 g iron bar cools from 94ºC to 5ºC?

$\Delta t = t_f - t_i$

$= 5 - 94 = -89c$

s of Fe = 0.444 J/g • ºC

$\Delta t = t_{final} - t_{initial} = 5^oC - 94^oC = -89^oC$

$q = ms\Delta t$ = 869 g x 0.444 J/g • ºC x –89ºC = -34,000 J

$q = m s \Delta t$

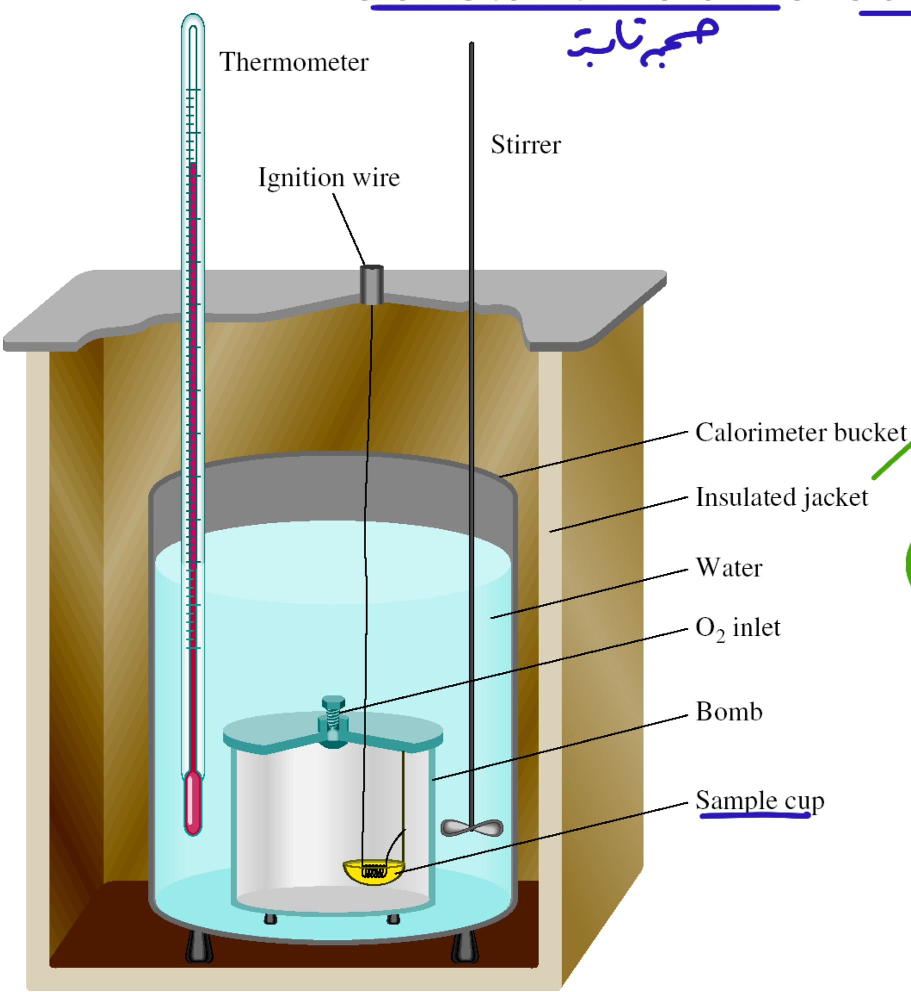
$q = 869 \times 0.444 \times -89$

$= -34000 J$

الاشارة سالبة تدل ان الطاقة مفقودة

Constant-Volume Calorimetry

حجم ثابت → مسعر حراري



$q_{sys} = q_{water} + q_{bomb} + q_{rxn}$

$q_{sys} = 0$

$q_{rxn} = -(q_{water} + q_{bomb})$

$q_{water} = m \times s \times \Delta t$

$q_{bomb} = C_{bomb} \times \Delta t$

Reaction at Constant *V*

$\Delta H \neq q_{rxn}$

$\Delta H \sim q_{rxn}$

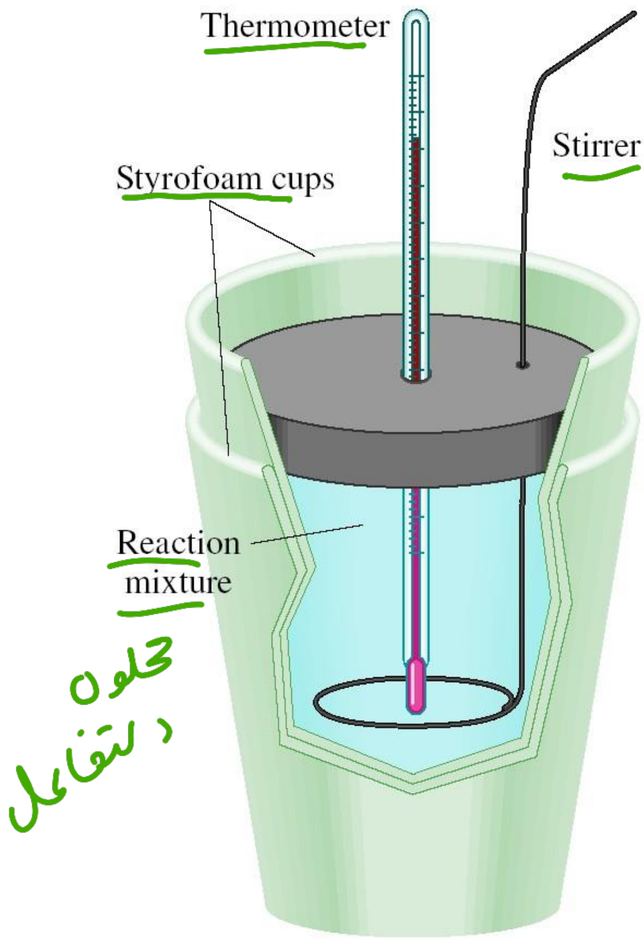
No heat enters or leaves!

الطاقة الي بنتجها التفاعل = الطاقة التي تكتسبها الوعاء bomb (q_{bomb}) + الطاقة التي تكتسبها الماء (q_{water})

$$-\left(ms\Delta T_{water} + C\Delta T_{bomb}\right) = q_{rxn}$$

$$\Delta H \approx q_{rxn}$$

Constant-Pressure Calorimetry



$q_{sys} = q_{water} + q_{cal} + q_{rxn}$

$q_{sys} = 0$

$q_{rxn} = -(q_{water} + q_{cal})$

$q_{water} = m \times s \times \Delta t$

$q_{cal} = C_{cal} \times \Delta t$

Reaction at Constant P

$\Delta H = q_{rxn}$

No heat enters or leaves!

TABLE 6.3 Heats of Some Typical Reactions Measured at Constant Pressure

Type of Reaction	Example	ΔH (kJ/mol)
Heat of neutralization	$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$	−56.2
Heat of ionization	$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$	56.2
Heat of fusion	$H_2O(s) \longrightarrow H_2O(l)$	6.01
Heat of vaporization	$H_2O(l) \longrightarrow H_2O(g)$	44.0*
Heat of reaction	$MgCl_2(s) + 2Na(l) \longrightarrow 2NaCl(s) + Mg(s)$	−180.2

*Measured at 25°C. At 100°C, the value is 40.79 kJ.

Chemistry in Action:

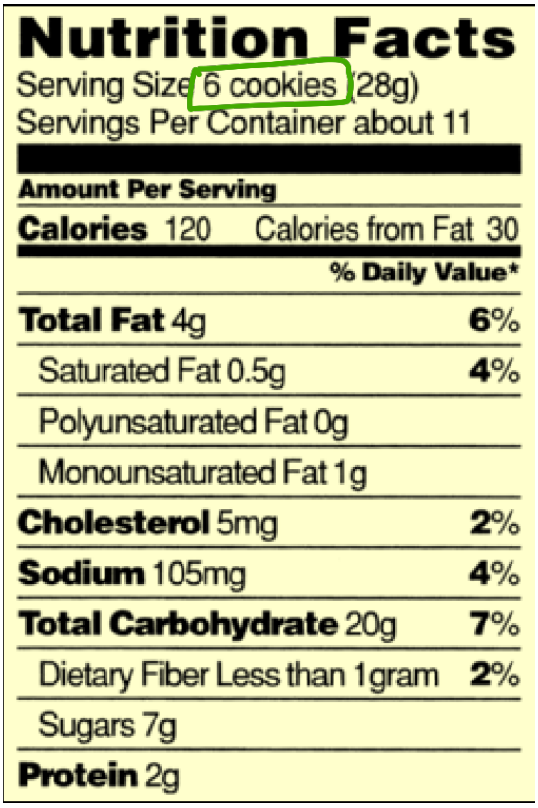
Fuel Values of Foods and Other Substances

$$C_6H_{12}O_6\,(s) + 6O_2\,(g) \longrightarrow 6CO_2\,(g) + 6H_2O\,(l) \quad \Delta H = -2801 \text{ kJ/mol}$$

1 cal = 4.184 J

1 Cal = 1000 cal = 4184 J

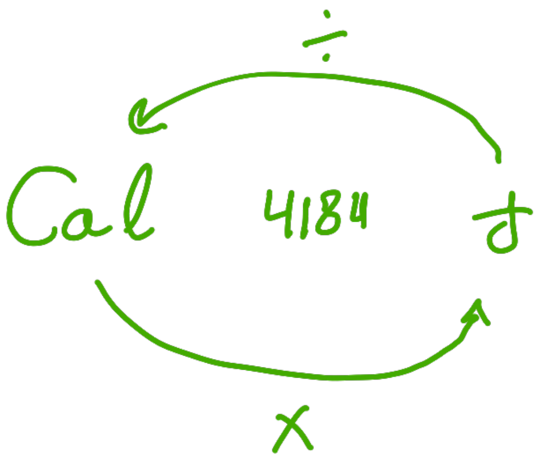
Substance	$\Delta H_{combustion}$ (kJ/g)
Apple	-2
Beef	-8
Beer	-1.5
Gasoline	-34

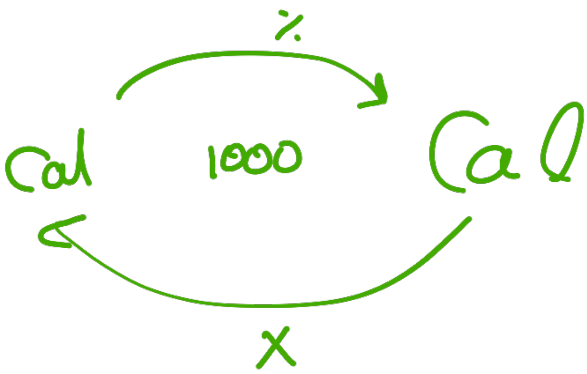


Nutrition Facts
Serving Size 6 cookies (28g)
Servings Per Container about 11

Amount Per Serving

Calories 120	Calories from Fat 30
	% Daily Value*
Total Fat 4g	**6%**
Saturated Fat 0.5g	**4%**
Polyunsaturated Fat 0g	
Monounsaturated Fat 1g	
Cholesterol 5mg	**2%**
Sodium 105mg	**4%**
Total Carbohydrate 20g	**7%**
Dietary Fiber Less than 1gram	**2%**
Sugars 7g	
Protein 2g	





Standard Enthalpy of Formation and Reaction

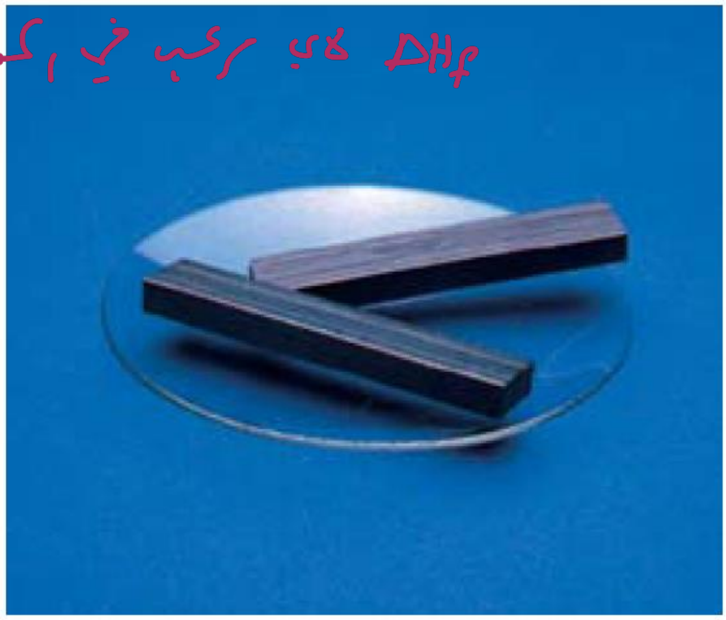
Because there is no way to measure the absolute value of the enthalpy of a substance, must I measure the enthalpy change for every reaction of interest?

Establish an arbitrary scale with the **standard enthalpy of formation** (ΔH^0_f) as a reference point for all enthalpy expressions.

Standard enthalpy of formation (ΔH^0_f) is the heat change that results when **one mole** of a compound is formed from its **elements** at a pressure of 1 atm.

ΔHf لأي مركب في أكثر حالاته استقراراً = صفر

The standard enthalpy of formation of any element in its most stable form is zero.



$\Delta H_f^0 (O_2) = 0$

$\Delta H_f^0 (O_3) = 142$ kJ/mol

ΔH_f^0 (C, graphite) = 0

ΔH_f^0 (C, diamond) = 1.90 kJ/mol

ΔH_f^0 للعناصر في الجدول الدوري = صفر

ΔH_f^0 للغازات الموجودة على شكل جزيئات في الطبيعة = صفر

TABLE 6.4 Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	ΔH_f°(kJ/mol)	Substance	ΔH_f°(kJ/mol)
$Ag(s)$	0	$H_2O_2(l)$	−187.6
$AgCl(s)$	−127.0	$Hg(l)$	0
$Al(s)$	0	$I_2(s)$	0
$Al_2O_3(s)$	−1669.8	$HI(g)$	25.9
$Br_2(l)$	0	$Mg(s)$	0
$HBr(g)$	−36.2	$MgO(s)$	−601.8
C(graphite)	0	$MgCO_3(s)$	−1112.9
C(diamond)	1.90	$N_2(g)$	0
$CO(g)$	−110.5	$NH_3(g)$	−46.3
$CO_2(g)$	−393.5	$NO(g)$	90.4
$Ca(s)$	0	$NO_2(g)$	33.85
$CaO(s)$	−635.6	$N_2O(g)$	81.56
$CaCO_3(s)$	−1206.9	$N_2O_4(g)$	9.66
$Cl_2(g)$	0	$O(g)$	249.4
$HCl(g)$	−92.3	$O_2(g)$	0
$Cu(s)$	0	$O_3(g)$	142.2
$CuO(s)$	−155.2	S(rhombic)	0
$F_2(g)$	0	S(monoclinic)	0.30
$HF(g)$	−271.6	$SO_2(g)$	−296.1
$H(g)$	218.2	$SO_3(g)$	−395.2
$H_2(g)$	0	$H_2S(g)$	−20.15
$H_2O(g)$	−241.8	$Zn(s)$	0
$H_2O(l)$	−285.8	$ZnO(s)$	−348.0

$$aA + bB \longrightarrow cC + dD$$

$$\Delta H^\circ_{rxn} = \left[\text{الطاقة الحرارية للتكوين } \sum \Delta H_f^\circ \text{ النواتج}\right] - \left[\text{الطاقة الحرارية للتكوين } \sum \Delta H_f^\circ \text{ المتفاعلات}\right]$$

$$\Delta H^\circ_{rxn} = \left[c\Delta H_f^\circ(C) + d\Delta H_f^\circ(D)\right] - \left[a\Delta H_f^\circ(A) + b\Delta H_f^\circ(B)\right]$$

The **standard enthalpy of reaction** (ΔH^0_{rxn}) is the enthalpy of a reaction carried out at 1 atm.

$$aA + bB \longrightarrow cC + dD$$

$$\Delta H^0_{rxn} = [c\Delta H^0_f(C) + d\Delta H^0_f(D)] - [a\Delta H^0_f(A) + b\Delta H^0_f(B)]$$

$$\Delta H^0_{rxn} = \Sigma n\Delta H^0_f(\text{products}) - \Sigma m\Delta H^0_f(\text{reactants})$$

نواتج متفاعلات

Hess's Law: When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

(Enthalpy is a state function. It doesn't matter how you get there, only where you start and end.)

⋆ (1) Calculate standard enthalpy of reaction.

$$Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2(g)}$$

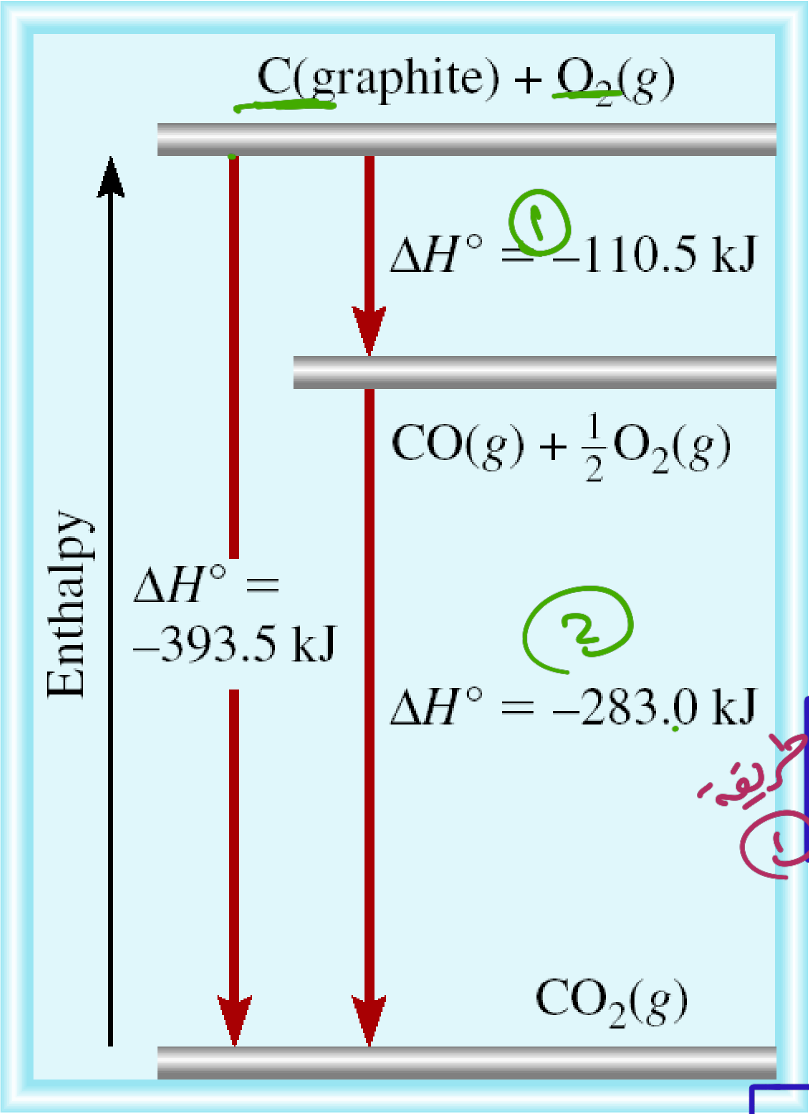
from the following data.

$$\Delta_f H^0_{Fe_2O_3} = -824\ \text{kJ/mol}$$
$$\Delta_f H^0_{CO} = -110\ \text{kJ/mol}$$
$$\Delta_f H^0_{CO_2} = -393\ \text{kJ/mol}$$

$$\Delta H^0_{rxn} = [2\Delta H_f(Fe) + 3\Delta H_f(CO_2)] - [\Delta H_f(Fe_2O_3) + 3\Delta H_f(CO)]$$

$$= [3(-393)] - [-824 + 3(-110)]$$

$$= 25\ \text{kJ/mol}$$



$$C\ (\text{graphite}) + 1/2O_2\ (g) \longrightarrow CO\ (g)$$

$$CO\ (g) + 1/2O_2\ (g) \longrightarrow CO_2\ (g)$$

$$C\ (\text{graphite}) + O_2\ (g) \longrightarrow CO_2\ (g)$$

طريقة ①

$$C_{\text{graph}} + O_{2\,(g)} \longrightarrow CO_2$$

$$\Delta H^\circ_{rnx} = -393.5 - [0]$$

$$\Delta H^\circ_{rnx} = -393.5$$

طريقة 2 نحسب طاقة كل تفاعل و نجمع التفاعلين

rxn ① $\Delta H_{rxn} = -110.5 - 0 = -110.5$

rxn ② $\Delta H_{rxn} = -393.5 - [-110.5] = -283$

ΔH_{rxn} ① + ② $= -393.5$

Calculate the standard enthalpy of formation of CS_2 (*l*) given that:

$$C(graphite) + O_2\ (g) \longrightarrow CO_2\ (g) \qquad \Delta H^0_{rxn} = -393.5\ kJ/mol$$

$$S(rhombic) + O_2\ (g) \longrightarrow SO_2\ (g) \qquad \Delta H^0_{rxn} = -296.1\ kJ/mol$$

$$CS_2(l) + 3O_2\ (g) \longrightarrow CO_2\ (g) + 2SO_2\ (g) \qquad \Delta H^0_{rxn} = -1072\ kJ/mol$$

1. Write the enthalpy of formation reaction for CS_2

$$C(graphite) + 2S(rhombic) \longrightarrow CS_2\ (l)$$

2. Add the given rxns so that the result is the desired rxn.

$$C(graphite) + O_2\ (g) \longrightarrow CO_2\ (g) \qquad \Delta H^0_{rxn} = -393.5\ kJ/mol$$

$$2S(rhombic) + 2O_2\ (g) \longrightarrow 2SO_2\ (g) \qquad \Delta H^0_{rxn} = -296.1\ kJ/mol \times 2$$

$$+ \quad CO_2(g) + 2SO_2\ (g) \longrightarrow CS_2\ (l) + 3O_2\ (g) \qquad \Delta H^0_{rxn} = +1072\ kJ/mol$$

$$C(graphite) + 2S(rhombic) \longrightarrow CS_2\ (l)$$

$$\Delta H^0_{rxn} = -393.5 + (2\times-296.1) + 1072 = 86.3\ kJ/mol$$

كتابة معادلة التكوين

$$C_{graphite} + 2S_{rhombic} \longrightarrow CS_2$$

نعكس معادلة رقم 3 ونجمع معها معادلة ① و معادلة ② مضروبة ب ②

$$CO_{2\,g} + 2SO_{2\,g} \rightarrow CS_{2\,l} + 3O_{2\,g} \qquad +1072$$

$$C_{graphite} + O_{2g} \rightarrow CO_2 \qquad -393$$

$$2S_{rombic} + 2O_{2g} \rightarrow 2SO_{2g} \qquad -296.1\times2$$

$$C_{graphite} + 2S_{rhomic} \rightarrow CS_{2\,l} \qquad \Delta H_{rxn} = 86.8\ kJ/mol$$

Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. How much heat is released per mole of benzene combusted? The standard enthalpy of formation of benzene is 49.04 kJ/mol.

$\Delta H_f^\circ (C_6H_6)$

$$2C_6H_6 (l) + 15O_2 (g) \longrightarrow 12CO_2 (g) + 6H_2O (l)$$

$$\Delta H^0_{rxn} = \Sigma n\Delta H^0_f \text{(products)} - \Sigma m\Delta H^0_f \text{(reactants)}$$

$$\Delta H^0_{rxn} = [12\Delta H^0_f (CO_2) + 6\Delta H^0_f (H_2O)] - [2\Delta H^0_f (C_6H_6)]$$

$$\Delta H^0_{rxn} = [12\times -393.5 + 6\times -187.6] - [2\times 49.04] = -5946 \text{ kJ}$$

$$\frac{-5946 \text{ kJ}}{2 \text{ mol}} = -2973 \text{ kJ/mol } C_6H_6$$

$$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$$

31

$$\Delta H^\circ_{rxn} = \Sigma n \Delta H_f^\circ \text{(products)} - \Sigma m \Delta H_f^\circ \text{(reactants)}$$

$$\Delta H^\circ_{rxn} = [6\Delta H_f^\circ (H_2O) + 12\Delta H_f^\circ (CO_2)] - [2\Delta H_f^\circ (C_6H_6) + 15\Delta H_f^\circ O_2]$$

0

$$\Delta H^\circ_{rxn} = [6(-285.8) + 12(-393.5)] - 2(49.04)$$

$$\Delta H^\circ_{rxn} = -6936.8$$

2 (?)

$$\Delta H^\circ_{rxn} = -3267 \text{ KJ/mol}$$

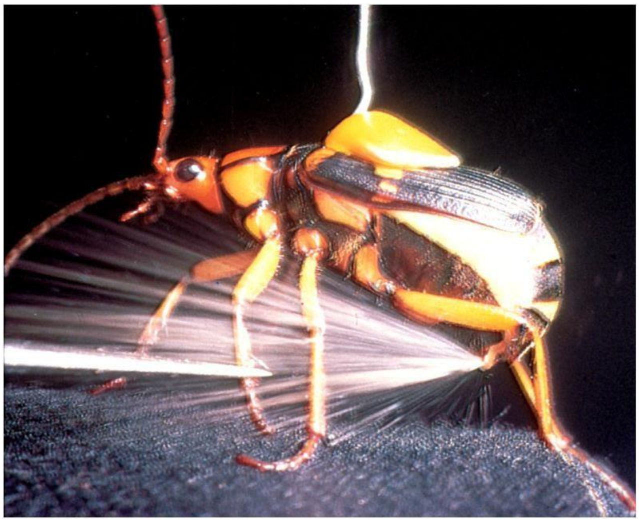
Chemistry in Action: Bombardier Beetle Defense

$C_6H_4(OH)_2\ (aq) + H_2O_2\ (aq) \longrightarrow C_6H_4O_2\ (aq) + 2H_2O\ (l)\ \Delta H^0 = ?$

$C_6H_4(OH)_2\ (aq) \longrightarrow C_6H_4O_2\ (aq) + H_2\ (g)\ \Delta H^0 = 177\ \text{kJ/mol}$ (1)

$H_2O_2\ (aq) \longrightarrow H_2O\ (l) + \frac{1}{2}O_2\ (g)\ \Delta H^0 = -94.6\ \text{kJ/mol}$ (2)

$H_2\ (g) + \frac{1}{2}O_2\ (g) \longrightarrow H_2O\ (l)\ \Delta H^0 = -286\ \text{kJ/mol}$ (3)



$\Delta H^0 = 177 - 94.6 - 286 = -204\ \text{kJ/mol}$

Exothermic!

نجمع التلات تفاعلات =

$C_6H_4(OH)_2(aq) + H_2O_2 + \cancel{H_2} + \cancel{\frac{1}{2}O_2}$

$\longrightarrow C_6H_4O_2 + \cancel{H_2} + H_2O$

$+ \cancel{\frac{1}{2}O_2} + H_2O$

$C_6H_4(OH)_2 + H_2O_2 \rightarrow C_6H_4O_2 + 2H_2O$

Table 3.10.1: Some Standard Enthalpies of Formation at 25°C.

Compound	ΔH_f/kJ mol^{-1}	ΔH_f/kcal mol^{-1}	Compound	ΔH_f/kJ mol^{-1}	ΔH_f/kcal mol^{-1}
$AgCl(s)$	−127.068	−30.35	$H_2O(g)$	−241.818	−57.79
$AgN_3(s)$	+620.6	+148.3	$H_2O(l)$	−285.8	−68.3
$Ag_2O(s)$	−31.0	−7.41	$H_2O_2(l)$	−187.78	−44.86
$Al_2O_3(s)$	−1675.7	−400.40	$H_2S(g)$	−20.63	−4.93
$Br_2(l)$	0.0	0.00	$HgO(s)$	−90.83	−21.70
$Br_2(g)$	+30.907	+7.385	$I_2(s)$	0.0	0.0
$C(s)$, graphite	0.0	0.00	$I_2(g)$	+62.438	+14.92
$C(s)$, diamond	+1.895	+0.453	$KCl(s)$	−436.747	−104.36
$CH_4(g)$	−74.81	−17.88	$KBr(s)$	−393.798	−94.097
$CO(g)$	−110.525	−26.41	$MgO(s)$	−601.7	−143.77
$CO_2(g)$	−393.509	−94.05	$NH_3(g)$	−46.11	−11.02
$C_2H_2(g)$	+226.73	+54.18	$NO(g)$	+90.25	+21.57
$C_2H_4(g)$	+52.26	+12.49	$NO_2(g)$	+33.18	+7.93
$C_2H_6(g)$	−84.68	−20.23	$N_2O_4(g)$	+9.16	+2.19
$C_6H_6(l)$	+49.03	+11.72	$NF_3(g)$	−124.7	−29.80
$CaO(s)$	−635.09	−151.75	$NaBr(s)$	−361.062	−86.28
$CaCO_3(s)$	−1206.92	−288.39	$NaCl(s)$	−411.153	−98.24
$CuO(s)$	−157.3	−37.59	$O_3(g)$	+142.7	+34.11
$Fe_2O_3(s)$	−824.2	−196.9	$SO_2(g)$	−296.83	−70.93
$HBr(g)$	−36.4	−8.70	$SO_3(g)$	−395.72	−94.56
$HCl(g)$	−92.307	−22.06	$ZnO(s)$	−348.28	−83.22
$HI(g)$	+26.48	+6.33			

The ***enthalpy of solution*** (**Δ*H*$_{soln}$**) is the heat generated or absorbed when a certain amount of solute dissolves in a certain amount of solvent.

$$\Delta H_{soln} = H_{soln} - H_{components}$$

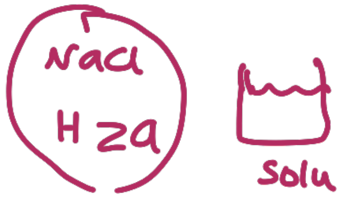


TABLE 6.5
Heats of Solution of Some Ionic Compounds

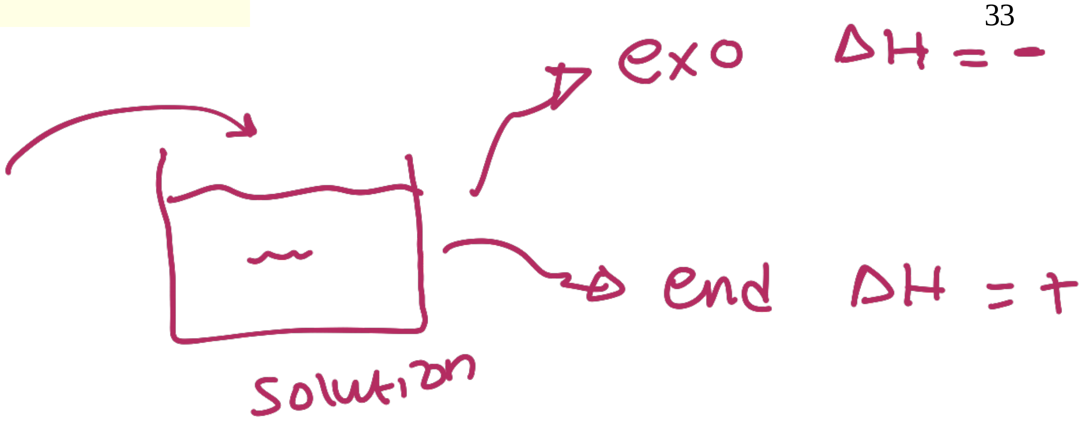
Compound		Δ*H*$_{soln}$ (kJ/mol)
LiCl	تسخين	−37.1
$CaCl_2$		−82.8
NaCl		4.0
KCl	تبريد	17.2
NH_4Cl		15.2
NH_4NO_3		26.2

Which substance(s) could be used for melting ice? ΔH=−

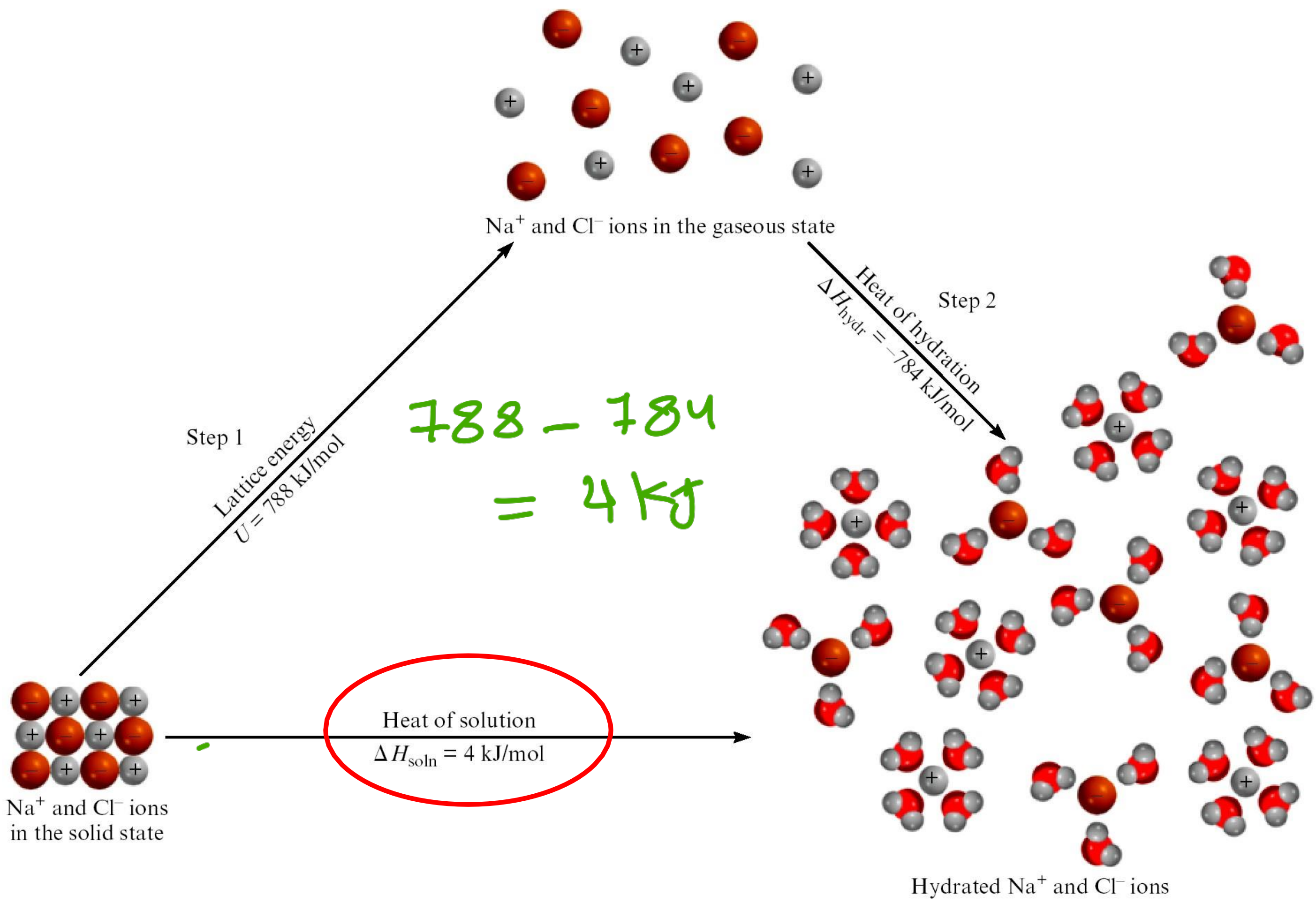
LiCl2 CaCl2

Which substance(s) could be used for a cold pack? ΔH=+

NH4NO3



The Solution Process for NaCl



ΔH_{soln} = Step 1 + Step 2 = 788 – 784 = 4 kJ/mol