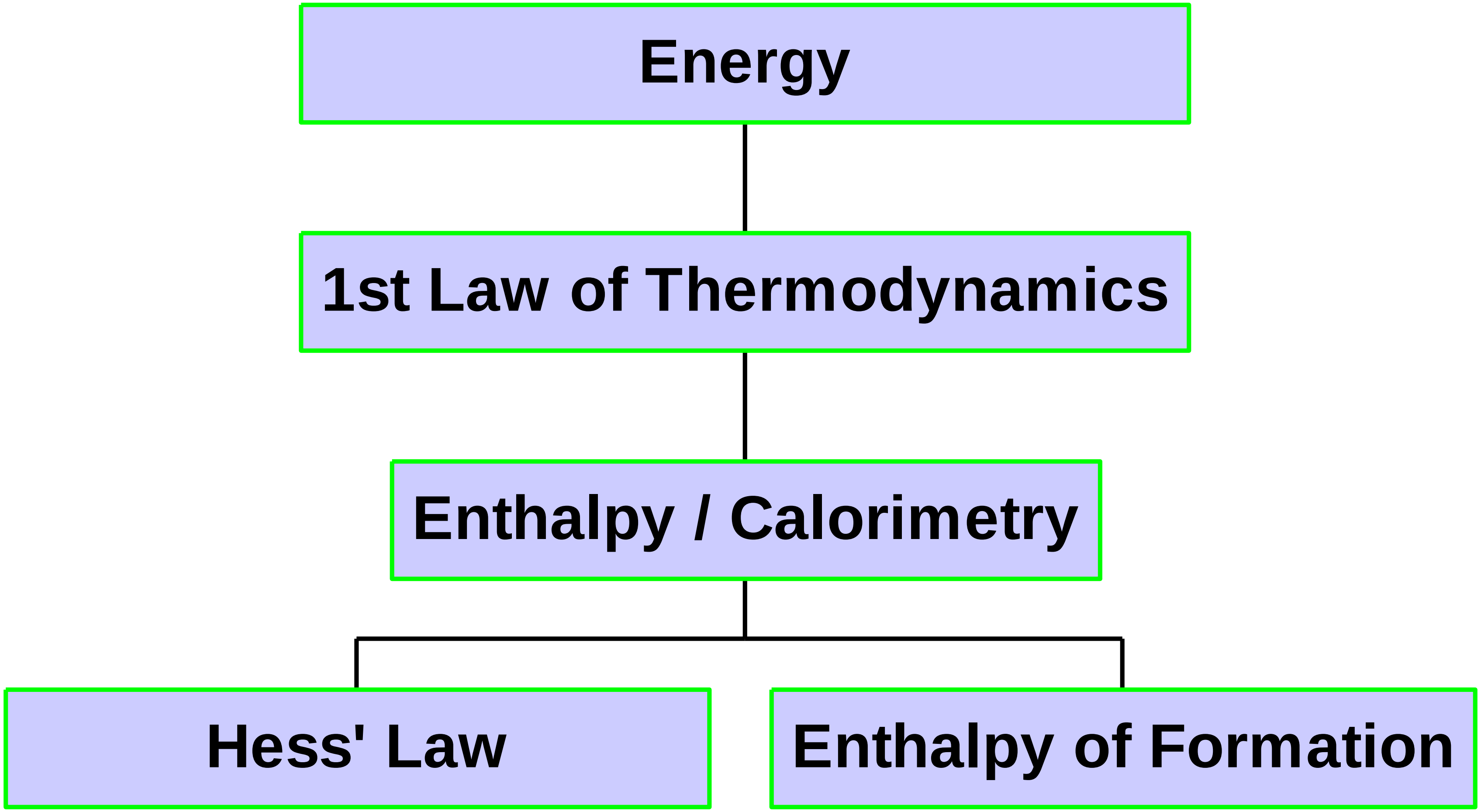
THERMOCHEMISTRY

Thermochemistry



Energy

1st Law of Thermodynamics

Enthalpy / Calorimetry

Hess' Law

Enthalpy of Formation

The Nature of Energy

Kinetic Energy and Potential Energy

- Kinetic energy is the energy of motion:

$$E_k = \frac{1}{2} \cdot m \cdot v^2$$

- Potential energy is the energy an object possesses by virtue of its position.
- Potential energy can be converted into kinetic energy. Example: a bicyclist at the top of a hill.

The Nature of Energy

Units of Energy

- SI Unit for energy is the joule, J:

$$E_k = \frac{1}{2} \cdot m \cdot v^2 = \frac{1}{2} \cdot (2\ \mathrm{kg}) \cdot (1\ \mathrm{m/s})^2$$

$$= 1\ \mathrm{kg\ m^2\ s^{-2}} = 1\ \mathrm{J}$$

sometimes the calorie is used instead of the joule:

1 cal = 4.184 J (exactly)

A nutritional Calorie:

1 Cal = 1000 cal = 1 kcal

Thermochemistry Terminology

- System: part of the universe we are interested in.
- Surrounding: the rest of the universe.
- Boundary: between system & surrounding.
- Exothermic: energy released by system to surrounding.
- Endothermic: energy absorbed by system from surr.

- Work (w): product of force applied to an object over a distance.

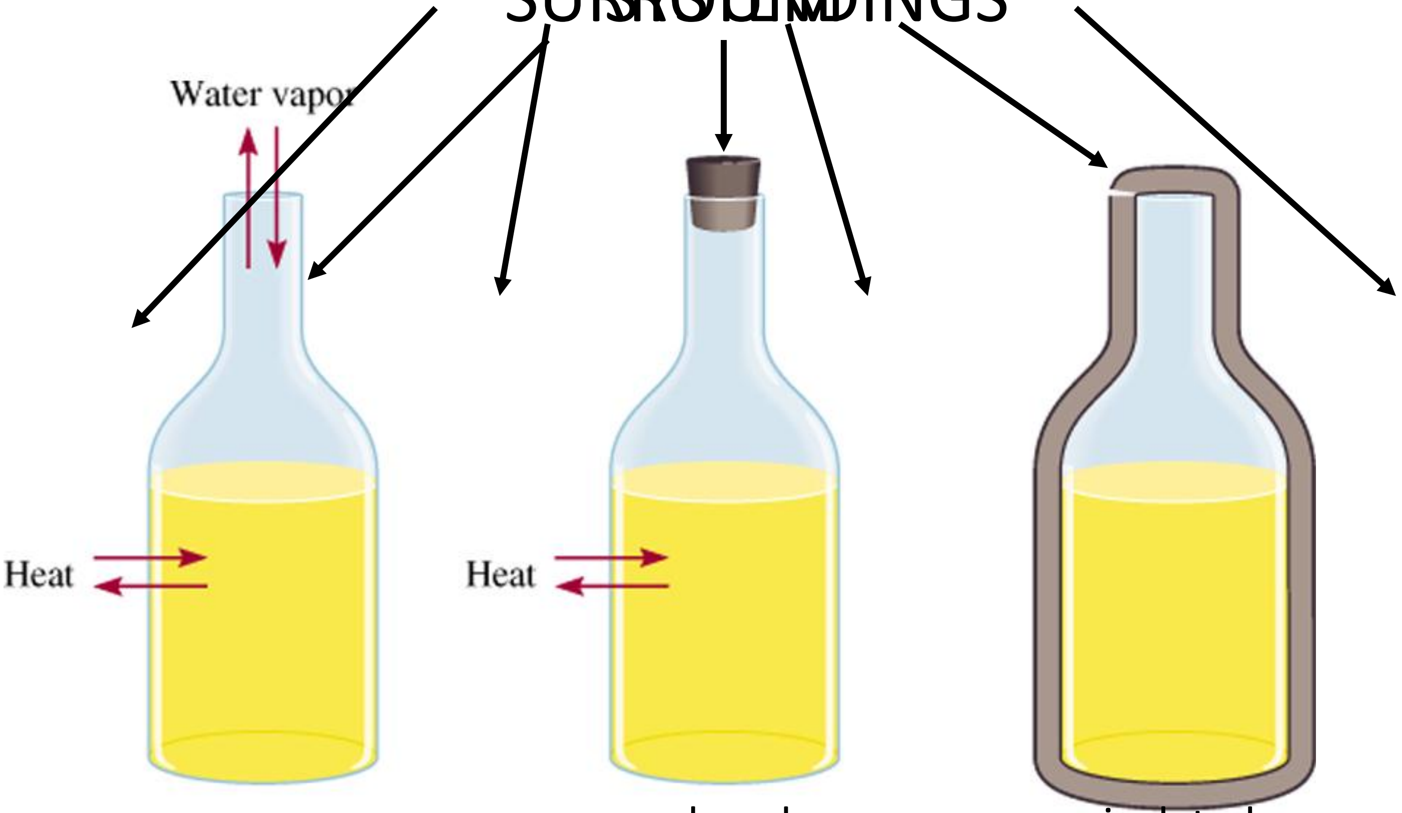
- Heat (q): transfer of energy between two objects

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.

SURROUNDINGS

SYSTEM



	open	closed	isolated
Exchange:	mass & energy	energy	nothing

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

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

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

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

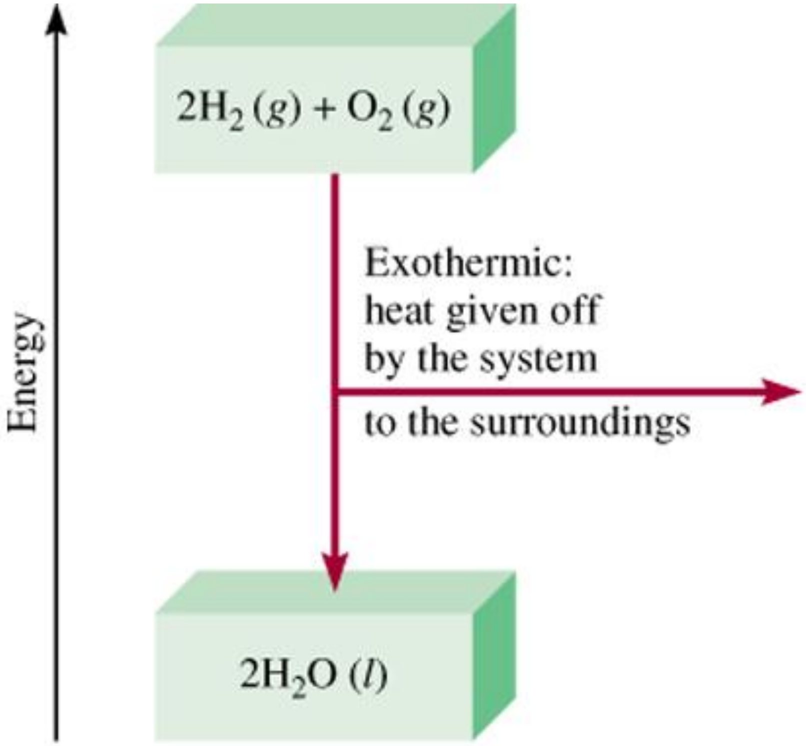
$$\text{energy} + 2HgO\,(s) \longrightarrow 2Hg\,(l) + O_2\,(g)$$

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

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

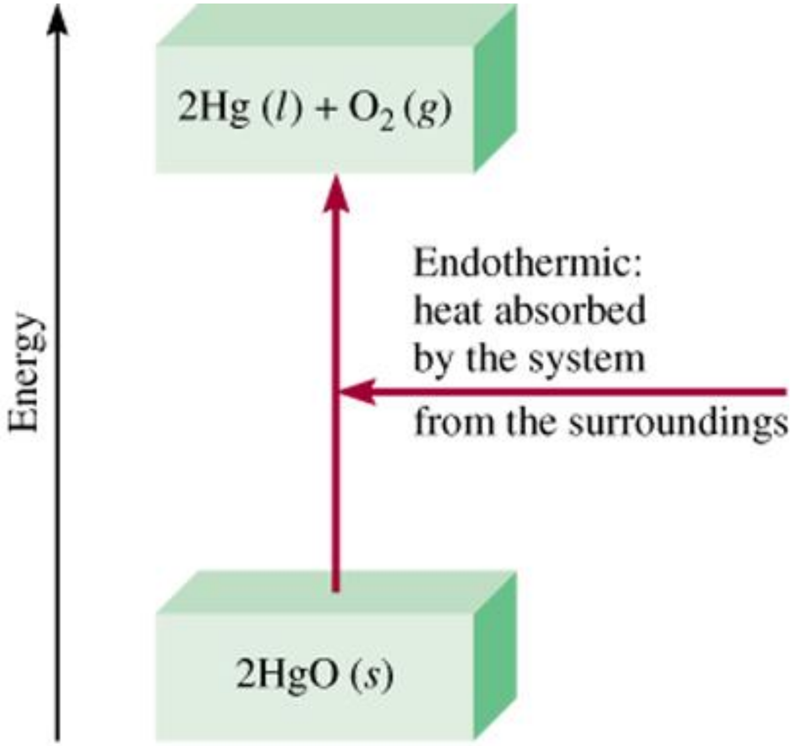
$$\Delta H = H\text{ (products)} - H\text{ (reactants)}$$

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



$H_{products} < H_{reactants}$

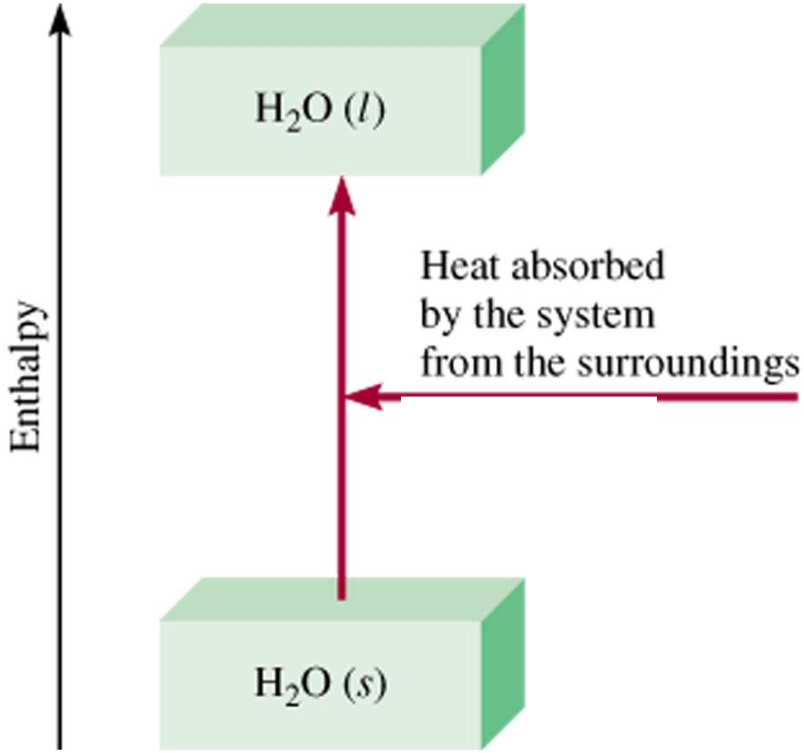
$\Delta H < 0$



$H_{products} > H_{reactants}$

$\Delta H > 0$

Thermochemical Equations



Is ΔH negative or positive?

System absorbs heat

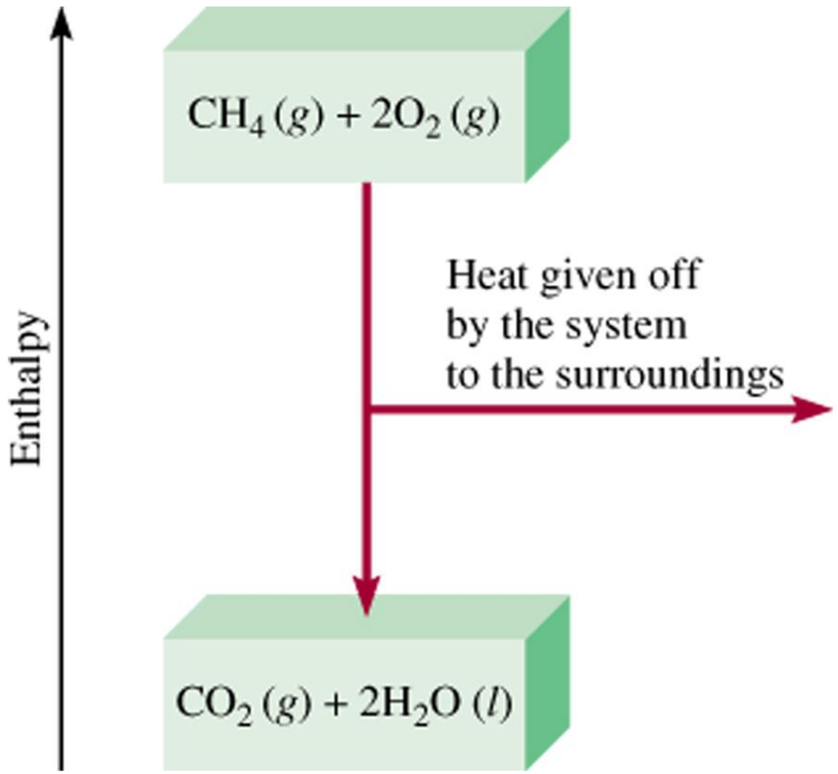
Endothermic

$\Delta H > 0$

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

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

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 25^0C and 1 atm.

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

Thermochemical Equations

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

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

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

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

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

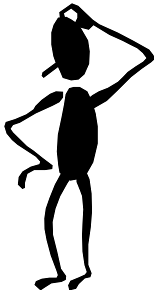
$$2H_2O\ (s) \longrightarrow 2H_2O\ (l) \qquad \Delta H = 2 \times 6.01 = 12.0 \text{ kJ}$$

Thermochemical Equations

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

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

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



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

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

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

QUIZ

For the decomposition of hydrogen peroxide, it is known that:

$H_2O_2(l) \rightarrow H_2O(l) + 1/2\ O_2(g)$; ΔH = -98.2 kJ

Using this information, determine ΔH for the reaction:

$2\ H_2O(l) + O_2(g) \rightarrow 2\ H_2O_2(l)$

When looking at the second equation, we see it is double the first reaction and in the opposite direction.

First change the direction of the first equation. When the direction of the reaction is changed, the sign on ΔH changes for the reaction

$H_2O_2(l) \rightarrow H_2O(l) + 1/2\ O_2(g)$; $\Delta H = -98.2$ kJ

; becomes

$H_2O(l) + 1/2\ O_2(g) \rightarrow H_2O_2(l)$; $\Delta H = +98.2$ kJ

Second, multiply this reaction by 2. When multiplying a reaction by a constant, the ΔH is multiplied by the same constant.

$2\ H_2O(l) + O_2(g) \rightarrow 2\ H_2O_2(l)$; $\Delta H = +196.4$ kJ

Answer

$\Delta H = +196.4$ kJ for the reaction: $2\ H_2O(l) + O_2(g) \rightarrow 2\ H_2O_2(l)$

The First Law of Thermodynamics

Internal Energy

- Internal Energy: total energy of a system.
- Involves translational, rotational, vibrational motions.
- Cannot measure absolute internal energy.
- Change in internal energy,

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

$DE > 0$ Increase in energy of system
(gained from surroundings)
$DE < 0$ Decrease in energy of system
(lost to surroundings)

The First Law of Thermodynamics

Relating ΔE to Heat(q) and Work(w)

- Energy cannot be created or destroyed.
- Energy of (system + surroundings) is constant.
- Any energy transferred from a system must be transferred to the surroundings (and *vice versa*).

- From the first law of thermodynamics:

$$\Delta E = q + w$$

- When a system undergoes a chemical or physical change, the change in **internal energy (E) is equal to the heat (q)** added or liberated from the system **plus the work (w)** done on or by the system:

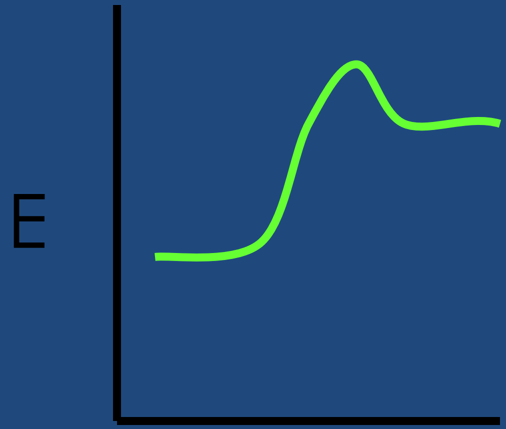
$$\Delta E = q + w$$

Sign Conventions (Table 5.1)

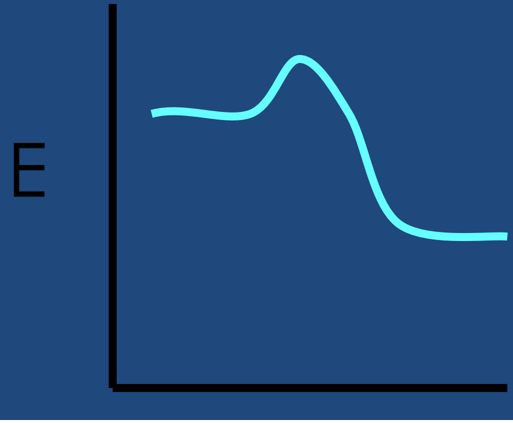
$q > 0$	Heat is added to system
$q < 0$	Heat is removed from system (into surroundings)
$w > 0$	Work done to system
$w < 0$	System does work on surroundings

Heat & reactions

- ***Endothermic:*** energy added to system, + ΔE



- ***Exothermic:*** energy exits system, - ΔE



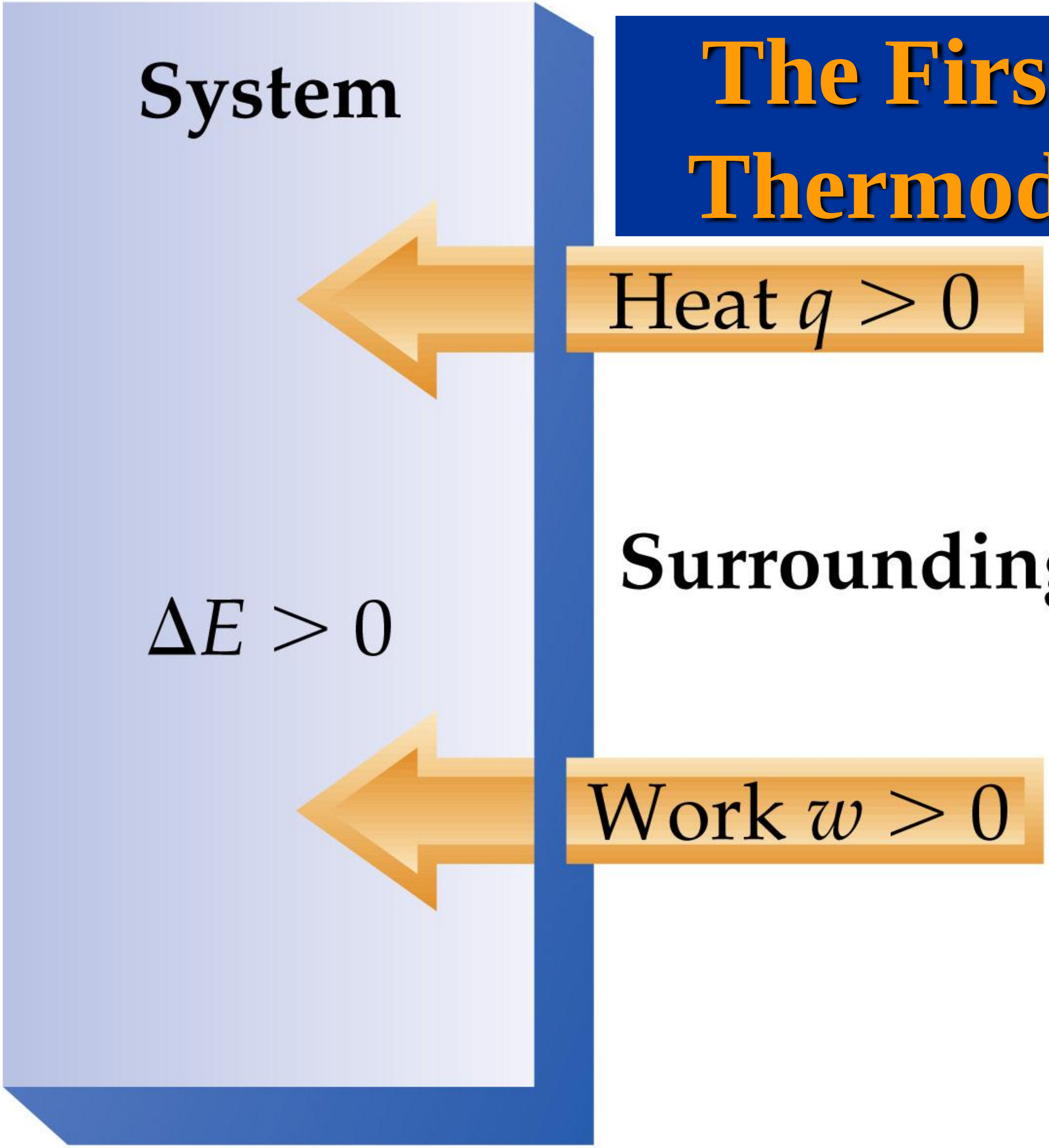
Example:

- Octane and oxygen gases combust within a closed cylinder in an engine. The cylinder absorbs 1150 J of heat and a piston is pushed down by 480 J during the reaction. What is the change in internal energy of the system?
  - q is (-) since heat leaves system; w is (-) since work is done by system. Therefore,

    $\Delta E = q + w = (-1150\ J) + (-480\ J) = -\ 1630\ J$

  - 1630 J has been liberated from the system (C_8H_{18} and O_2) added to the surroundings (engine, atmosphere, etc.)

The First Law of Thermodynamics



The First Law of Thermodynamics

- Calculate the energy change for a system undergoing an exothermic process in which 15.4 kJ of heat flows and where 6.3 kJ of work is done on the system.

$$\Delta E = q + w$$

TABLE 5.1 Sign Conventions Used and the Relationship Among q, w, and ΔE

Sign Convention for q:	**Sign of $\Delta E = q + w$**
$q > 0$: Heat is transferred from the surroundings to the system	$q > 0$ and $w > 0$: $\Delta E > 0$
$q < 0$: Heat is transferred from the system to the surroundings	$q > 0$ and $w < 0$: The sign of ΔE depends on the magnitudes of q and w
Sign Convention for w:	$q < 0$ and $w > 0$: The sign of ΔE depends on the magnitudes of q and w
$w > 0$: Work is done by the surroundings on the system	$q < 0$ and $w < 0$: $\Delta E < 0$
$w < 0$: Work is done by the system on the surroundings	

The First Law of Thermodynamics

Exothermic and Endothermic Processes

- Endothermic: absorbs heat from the surroundings.
- An endothermic reaction feels cold.

- Exothermic: transfers heat to the surroundings.
- An exothermic reaction feels hot.

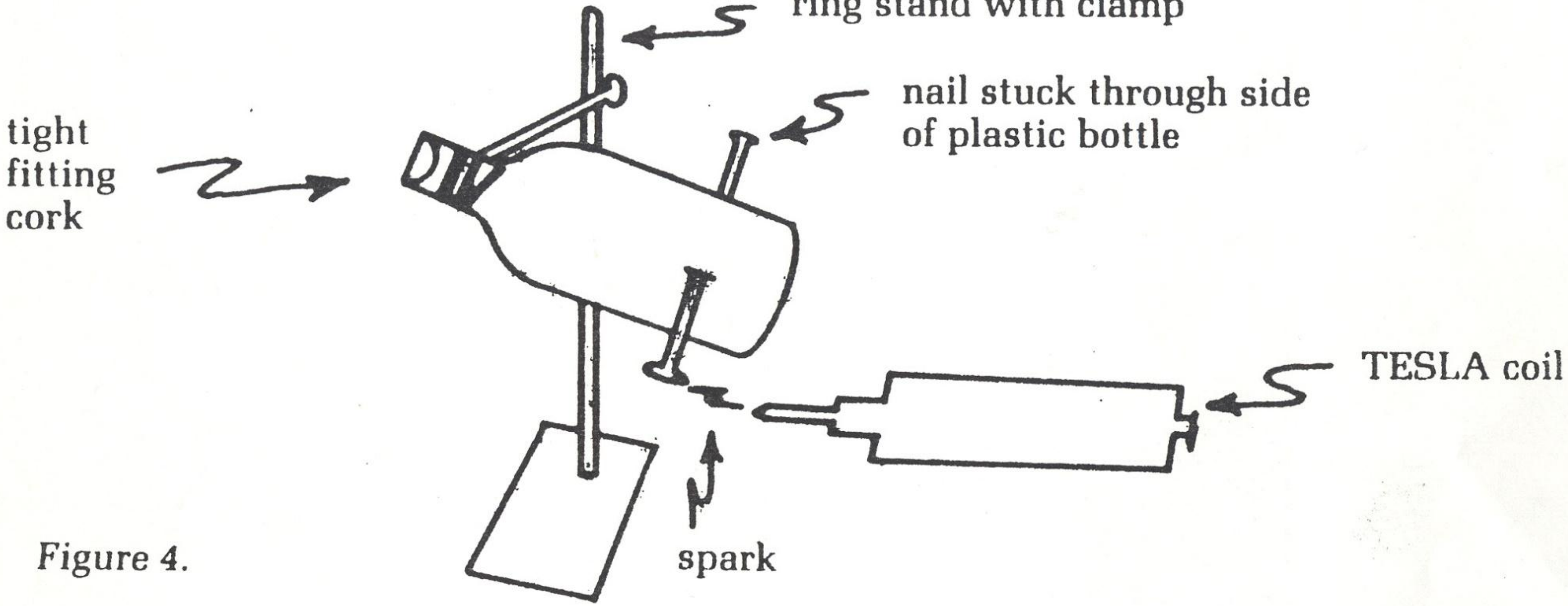


Figure 4.

$$2CH_3OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$$

Endothermic Reaction

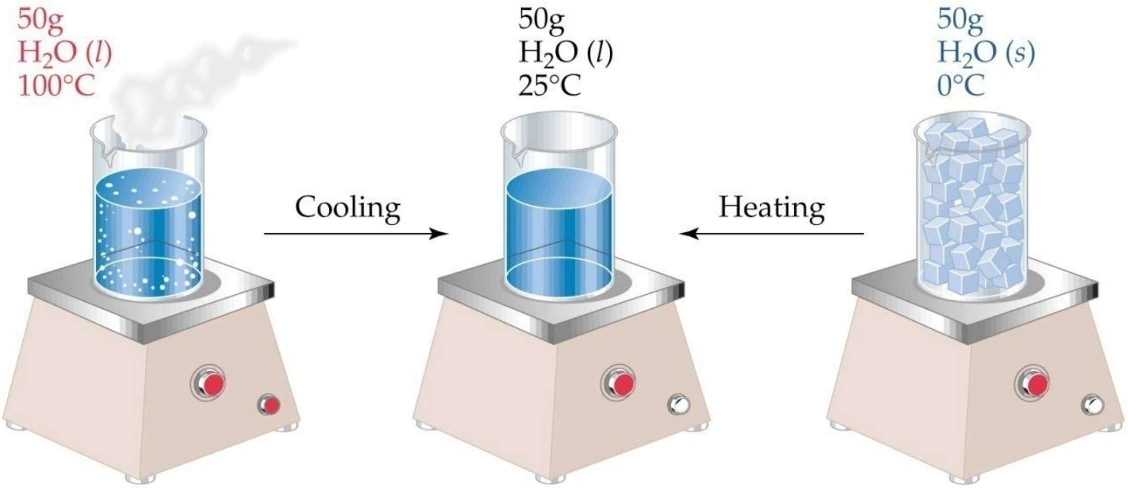
$Ba(OH)_2 \bullet 8H_2O(s) + 2\ NH_4SCN(s) \rightarrow$

$Ba(SCN)_2(s) + 2\ NH_3(g) + 10\ H_2O(l)$

The First Law of Thermodynamics

State Functions

- State function: depends only on the initial and final states of system, not on how the internal energy is used.



Enthalpy

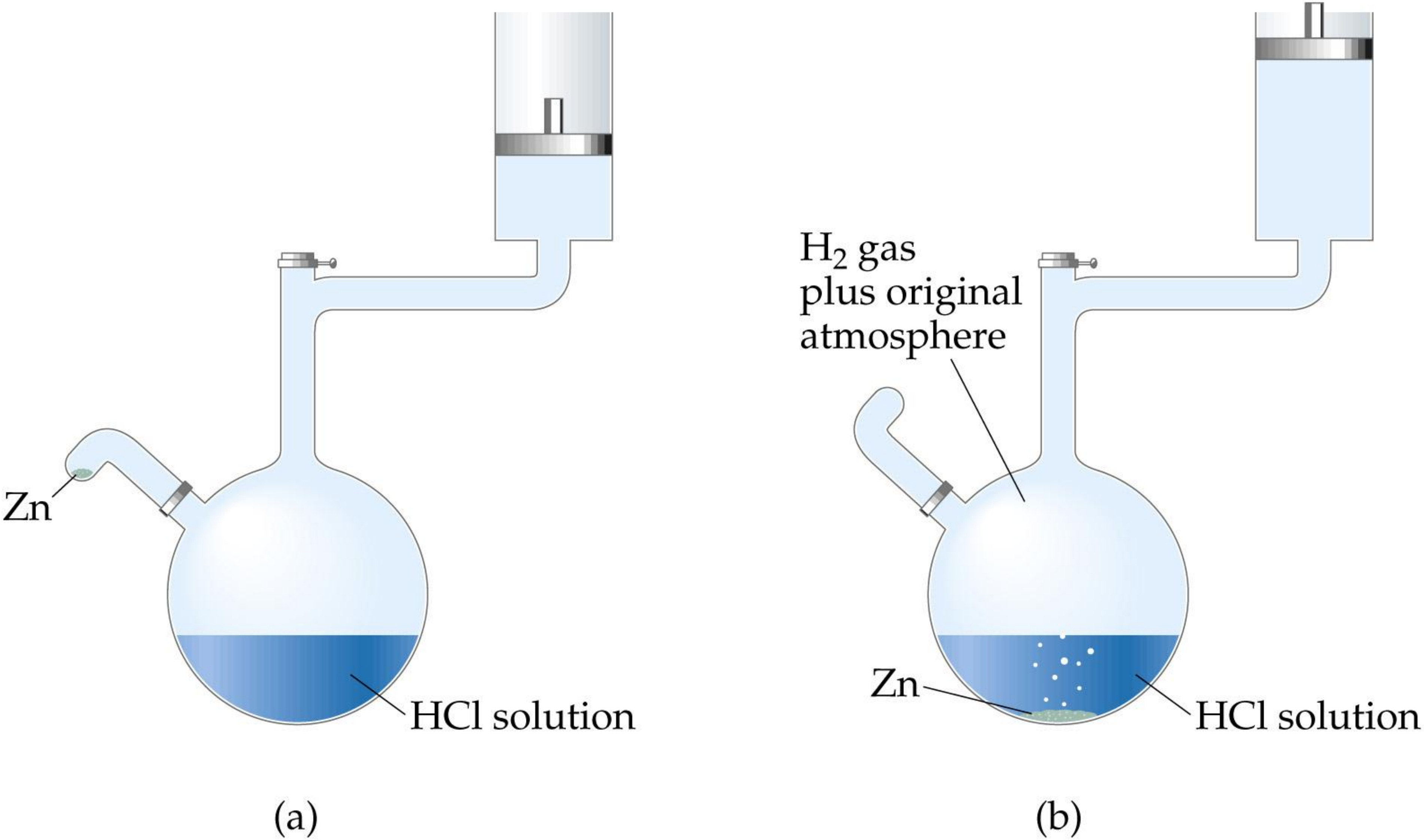
- Chemical reactions can absorb or release heat.
- However, they also have the ability to do work.
- For example, when a gas is produced, then the gas produced can be used to push a piston, thus doing work.

$$\mathrm{Zn}(s) + 2\mathrm{H}^+(aq) \rightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{H}_2(g)$$

- The work performed by the above reaction is called *pressure-volume* work.
- When the pressure is constant,

$$w = -P\Delta V$$

Enthalpy


Zn
HCl solution
(a)
H_2 gas
plus original
atmosphere
Zn
HCl solution
(b)

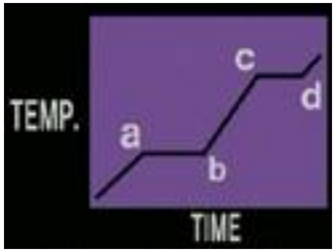
Enthalpy

- Enthalpy, *H*: Heat transferred between the system and surroundings carried out under constant pressure.

$$H = E + PV$$

- **Enthalpy is a state function.**
- If the process occurs at constant pressure,

$$\begin{aligned}\Delta H &= \Delta(E + PV)\\ &= \Delta E + P\Delta V\end{aligned}$$



Enthalpy

- Since we know that

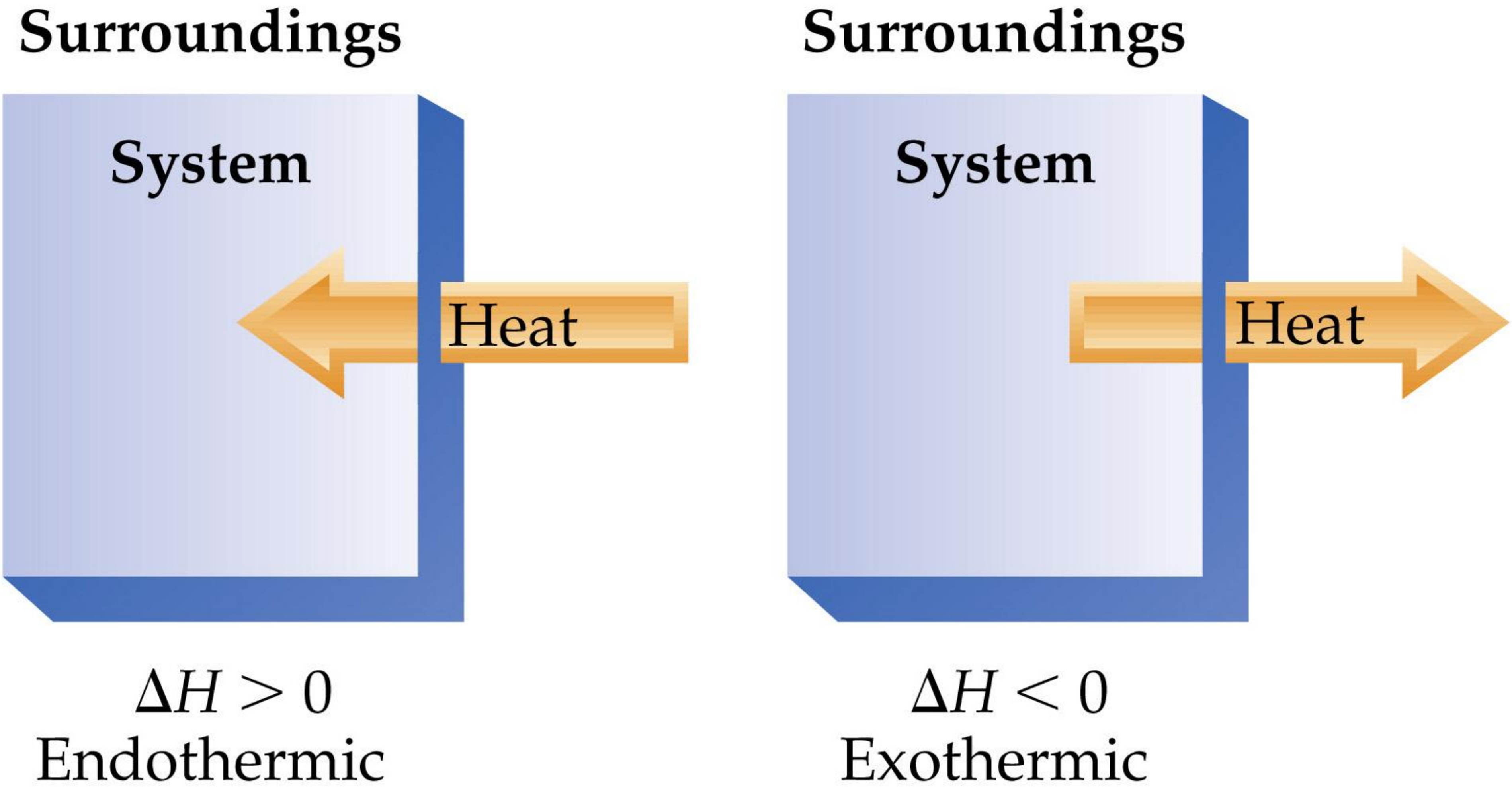
$$w = -P\Delta V$$

- We can write

$$\begin{aligned}\Delta H &= \Delta E + P\Delta V \\ &= q_P + w + P\Delta V \\ &= q_P + (-P\Delta V) + P\Delta V \\ &= q_P\end{aligned}$$

- When ΔH is positive, the system gains heat from the surroundings.
- When ΔH is negative, the surroundings gain heat from the system.

Enthalpy => Heat of Reaction



$\Delta H > 0$
Endothermic

$\Delta H < 0$
Exothermic

Enthalpies of Reaction

- For a reaction:

$$\begin{aligned}\Delta H &= H_{\text{final}} - H_{\text{initial}} \\ &= H_{\text{products}} - H_{\text{reactants}}\end{aligned}$$

- Enthalpy is an *extensive* property (magnitude ΔH is directly proportional to amount):

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \quad \Delta H = -802\ \text{kJ}$$

$$2CH_4(g) + 4O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g) \quad \Delta H = -1604\ \text{kJ}$$

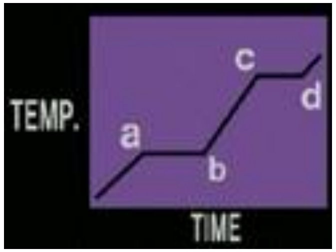
Enthalpies of Reaction

- When we reverse a reaction, we change the sign of ΔH:

$$CO_2(g) + 2H_2O(g) \rightarrow CH_4(g) + 2O_2(g) \quad \Delta H = +802\ \text{kJ}$$

- Change in enthalpy depends on state:

$$H_2O(g) \rightarrow H_2O(l) \quad \Delta H = -44\ \text{kJ}$$



Enthalpy Change of Water

Problem

Given: The heat of fusion of ice is 333 J/g (meaning 333 J is absorbed when 1 gram of ice melts). The heat of vaporization of liquid water at 100°C is 2257 J/g.

Part a: Calculate the change in enthalpy, ΔH, for these two processes.

$H_2O(s) \rightarrow H_2O(l)$; $\Delta H = ?$
$H_2O(l) \rightarrow H_2O(g)$; $\Delta H = ?$

Part b: Using the values you just calculated, determine the number of grams of ice that can be melted by 0.800 kJ of heat.

a.) Did you notice that the heats of fusion and vaporization were given in joules and not kilojoules? Using the periodic table, we know that 1 mole of water (H_2O) is 18.02 g. Therefore:

fusion $\Delta H = 18.02\text{ g} \times 333\text{ J} / 1\text{ g}$
fusion $\Delta H = 6.00 \times 10^3\text{ J}$
fusion $\Delta H = 6.00\text{ kJ}$

vaporization $\Delta H = 18.02\text{ g} \times 2257\text{ J} / 1\text{ g}$
vaporization $\Delta H = 4.07 \times 10^4\text{ J}$
vaporization $\Delta H = 40.7\text{ kJ}$

So, the completed thermochemical reactions are:

$H_2O(s) \rightarrow H_2O(l); \Delta H = +6.00\text{ kJ}$
$H_2O(l) \rightarrow H_2O(g); \Delta H = +40.7\text{ kJ}$

b.) Now we know that:

1 mol $H_2O(s)$ = 18.02 g $H_2O(s)$ ~ 6.00 kJ

Using this conversion factor:

0.800 kJ x 18.02 g ice / 6.00 kJ = 2.40 g ice melted

Answer
a.)
$H_2O(s) \rightarrow H_2O(l)$; $\Delta H = +6.00$ kJ
$H_2O(l) \rightarrow H_2O(g)$; $\Delta H = +40.7$ kJ

b.) 2.40 g ice melted

Calorimetry

Heat Capacity and Specific Heat

- Calorimetry = measurement of heat flow.
- Calorimeter = apparatus that measures heat flow.
- Heat capacity = the amount of energy required to raise the temperature of an object (by one degree).
- Molar heat capacity = heat capacity of 1 mol of a substance.
- Specific heat = specific heat capacity = heat capacity of 1 g of a substance.

$$q = (\text{specific heat}) \times (\text{grams of substance}) \times \Delta T$$

Table 5.2: Specific Heats (S) of Some Substances at 298 K

Substance	**S (J g^{-1} K^{-1})**
N_2(g)	1.04
Al(s)	0.902
Fe(s)	0.45
Hg(l)	0.14
H_2O(l)	4.184
H_2O(s)	2.06
CH_4(g)	2.20
CO_2(g)	0.84
Wood , Glass	1.76 , 0.84

If 24.2 kJ is used to warm a piece of aluminum with a mass of 250. g, what is the final temperature of the aluminum if its initial temperature is 5.0°C?

$$q = (\mathrm{S}) \times (\mathrm{m}) \times \Delta T$$

Problem

The following acid-base reaction is performed in a coffee cup calorimeter:

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

The temperature of 110 g of water rises from 25.0°C to 26.2°C when 0.10 mol of H^+ is reacted with 0.10 mol of OH^-.

- Calculate q_{water}
- Calculate ΔH for the reaction
- Calculate ΔH if 1.00 mol OH^- reacts with 1.00 mol H^+

HESS'S LAW

- States that if reaction is carried out in a series of steps, ΔH for the overal reaction will equal the sum of the enthalpy changes for the individual steps.

Bond Energies and Enthalpy Change

Determining the Change in Enthalpy of a Reaction

Problem

Estimate the change in enthalpy, ΔH, for the following reaction:

$H_2\ (g) + Cl_2\ (g) \rightarrow 2\ HCl\ (g)$

Solution

To work this problem, think of the reaction in terms of simple steps:

Step 1 The reactant molecules, H_2 and Cl_2, break down into their atoms

$H_2(g) \rightarrow 2\ H(g)$

$Cl_2(g) \rightarrow 2\ Cl(g)$

Step 2 These atoms combine to form HCl molecules

$2\ H\ (g) + 2\ Cl\ (g) \rightarrow 2\ HCl\ (g)$

In the first step, the H-H and Cl-Cl bonds are broken. In both cases, one mole of bonds is broken. When we look up the single bond energies for the H-H and Cl-Cl bonds, we find them to be +436 kJ/mol and + 243 kJ/mol, therefore for the first step of the reaction:

$\Delta H1 = +(436\ kJ + 243\ kJ) = +679\ kJ$

Bond breaking requires energy, so we expect the value for ΔH to be positive for this step.

In the second step of the reaction, two moles of H-Cl bonds are formed. Bond breaking liberates energy, so we expect the ΔH for this portion of the reaction to have a negative value. Using the table, the single bond energy for one mole of H-Cl bonds is found to be 431 kJ:

$\Delta H_2 = -2(431\ kJ) = -862\ kJ$

By applying Hess's Law, $\Delta H = \Delta H_1 + \Delta H_2$

$\Delta H = +679\ kJ - 862\ kJ$

$\Delta H = -183\ kJ$

Answer

The enthalpy change for the reaction will be $\Delta H = -183\ kJ$.