



Chapter 5

Thermochemistry

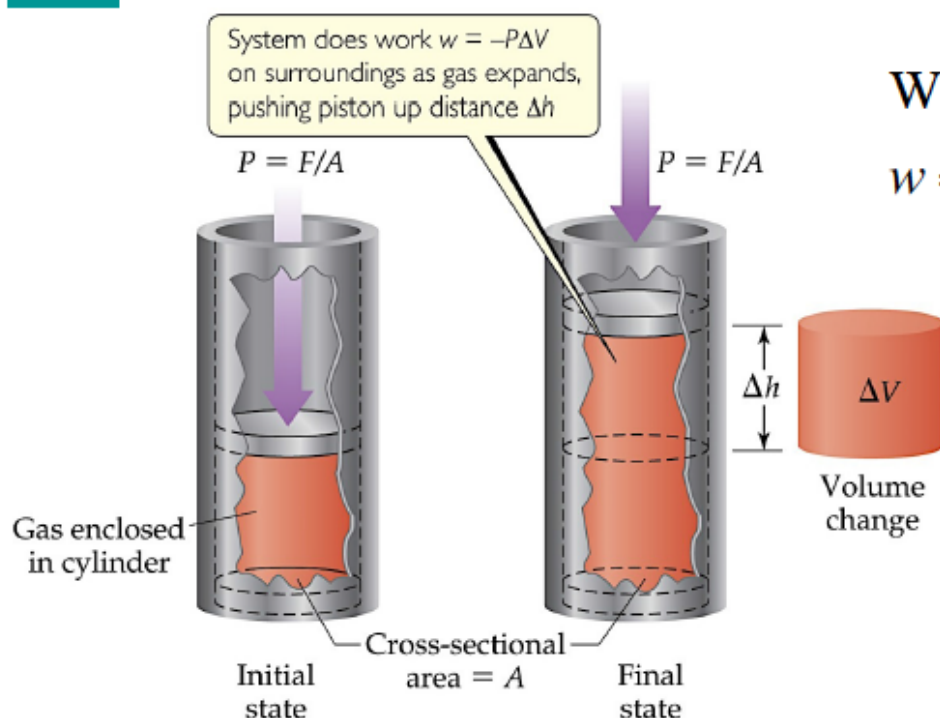
Energy

- **Energy** is the ability to do work or transfer heat.
 - Energy used to cause an object that has mass to move is called **work (w)**.
 - Energy used to cause the temperature of an object to rise is called **heat (q)**.

w and q are associated with changes or processes!

Work

Usually in an open container the only work done is by a gas pushing on the surroundings (or by the surroundings pushing on the gas).



$$\text{Work} = \text{force} \times \text{distance} = F \times \Delta h$$

$$w = (P \times A) \times \Delta h = P \times \Delta V$$

In expansion process, the energy of system is lowered by $P\Delta V$

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

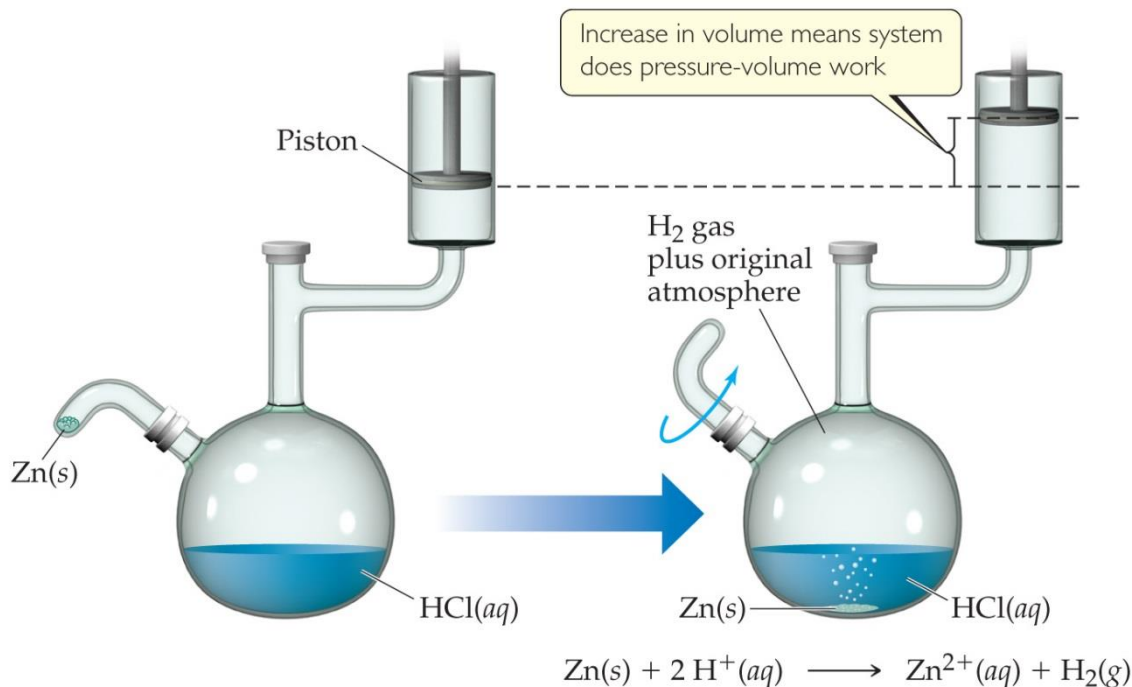
Work

We can measure the work done by the gas if the reaction is done in a vessel that has been fitted with a piston:

$$w = -P_{\text{ext}}\Delta V$$

External pressure

Increase in volume means system does pressure-volume work



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Units of Energy

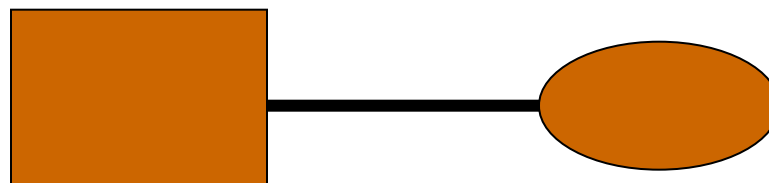
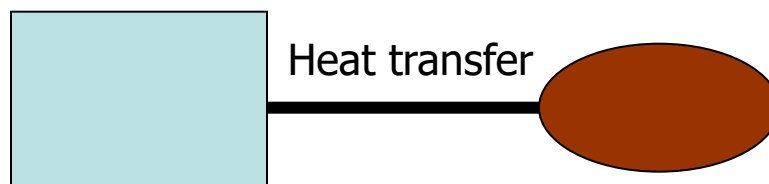
- The SI unit of energy is the **joule (J)**:

$$1 \text{ J} = 1 \frac{\text{kg m}^2}{\text{s}^2}$$

- An older, non-SI unit is still in widespread use: the **calorie (cal)**:

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

Zeroth Law of Thermodynamics

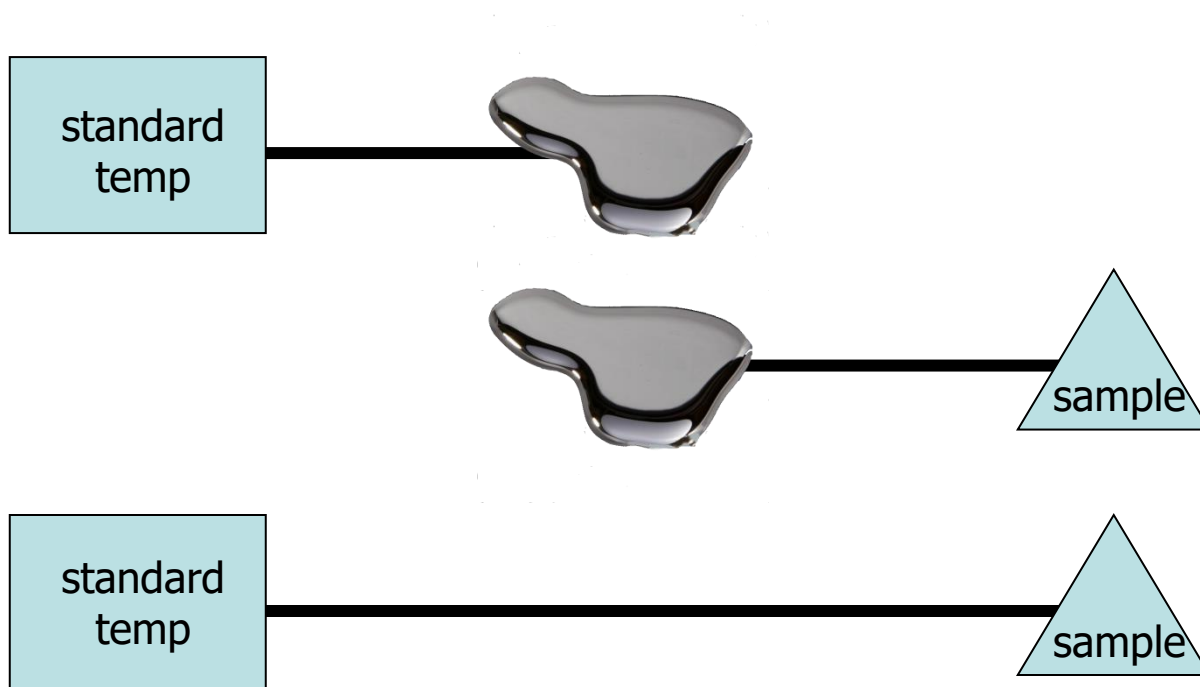


Thermal Equilibrium

Same Temperature

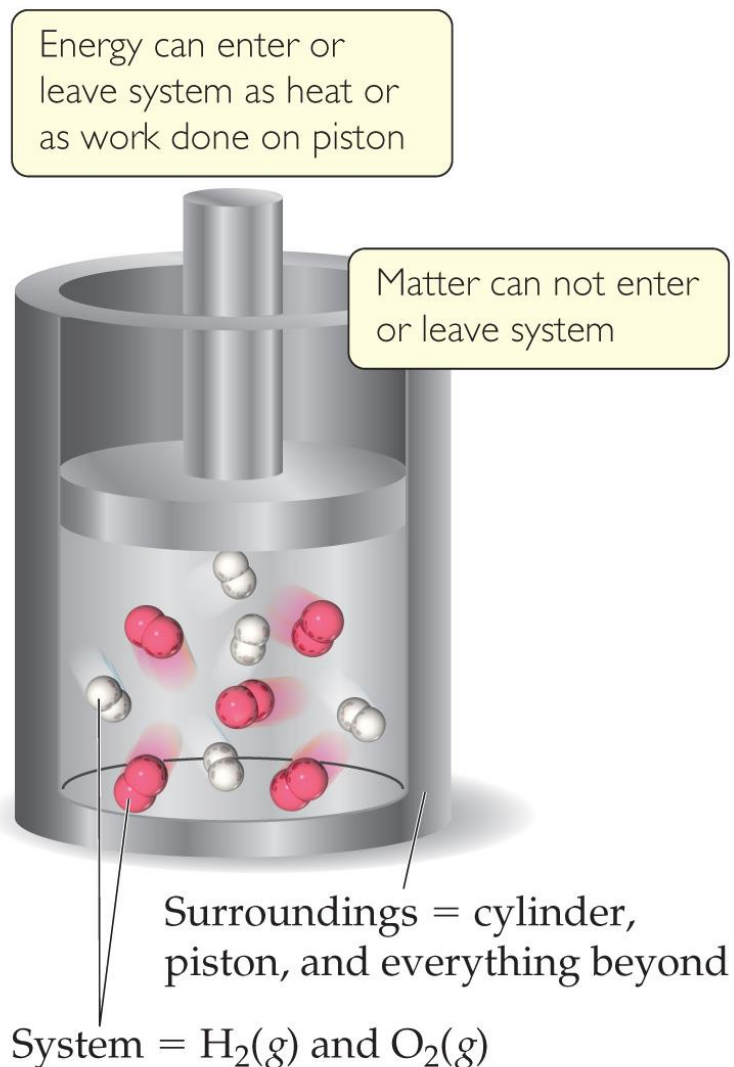
Equilibrium – unchanged with time

Zeroth Law of Thermodynamics



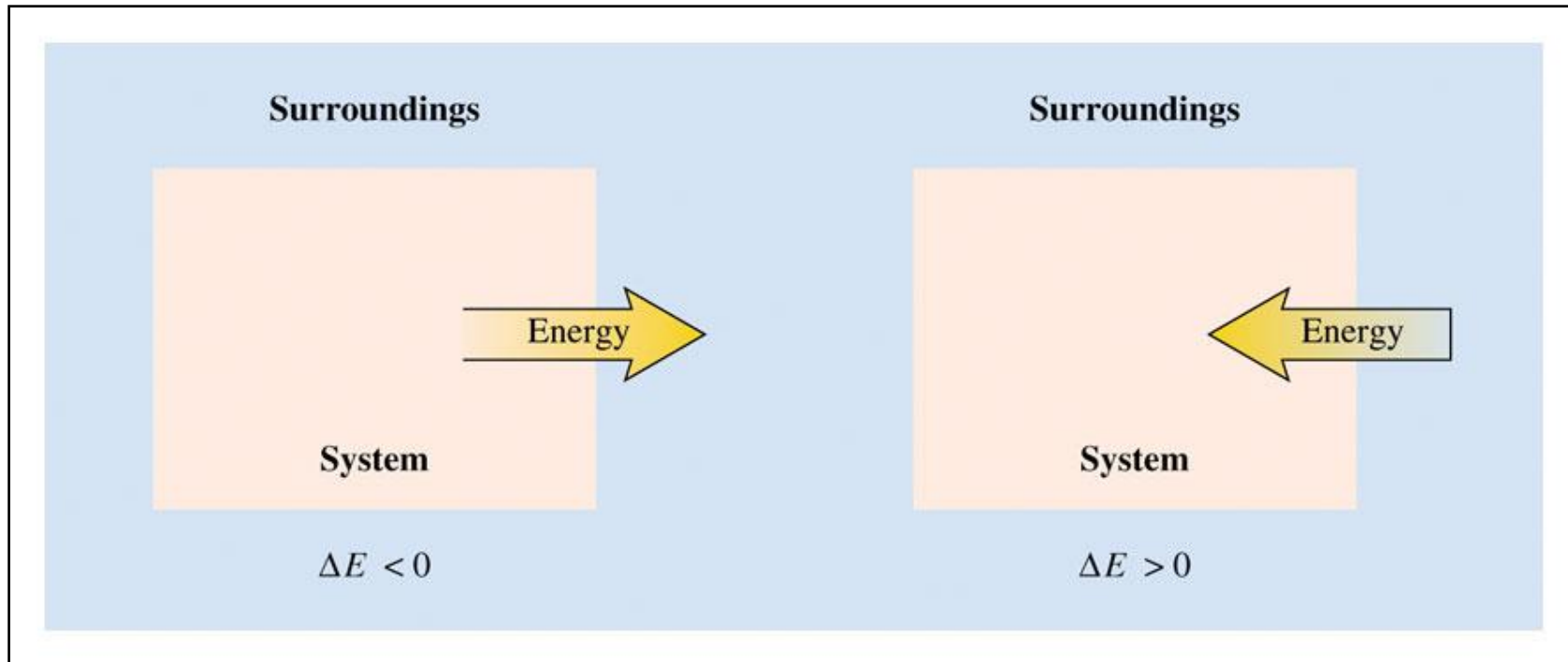
That's the principle of thermometer

System and Surroundings



- The **system** includes the molecules we want to study (here, the hydrogen and oxygen molecules).
- The **surroundings** are everything else (here, the cylinder and piston).

System and Surroundings



We take the system's point of view.

Exchange of Heat between System and Surroundings

- When heat is absorbed by the system from the surroundings, the process is **endothermic**.



Exchange of Heat between System and Surroundings

- When heat is absorbed by the system from the surroundings, the process is **endothermic**.
- When heat is released by the system into the surroundings, the process is **exothermic**.



First Law of Thermodynamics

- Energy is neither created nor destroyed.
- In other words, the total energy of the universe is a constant; if the system loses energy, it must be gained by the surroundings, and vice versa.

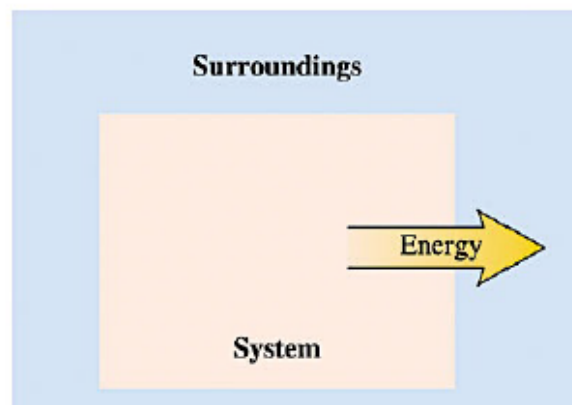
$$E_{\text{system}} + E_{\text{surrounding}} = E_{\text{universe}} = \text{constant}$$

Energy may exist in a form of which we are not aware yet!



First Law of Thermodynamics

- Energy is neither created nor destroyed.
- In other words, the total energy of the universe is a constant; if the system loses energy, it must be gained by the surroundings, and vice versa.



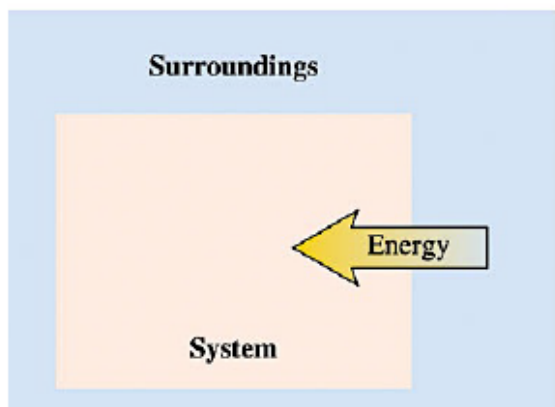
$$\Delta E_{sys} < 0$$

$$\Delta E_{sur} > 0$$

$$E_{\text{system}} + E_{\text{surrounding}} = \text{constant}$$

First Law of Thermodynamics

- Energy is neither created nor destroyed.
- In other words, the total energy of the universe is a constant; if the system loses energy, it must be gained by the surroundings, and vice versa.



$$\Delta E_{sys} > 0$$

$$\Delta E_{sur} < 0$$

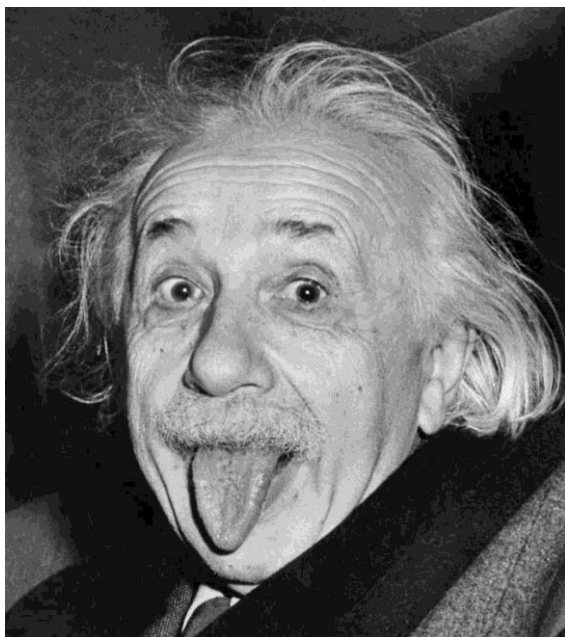
energy = heat + work

$$\Delta E = q + w$$

$$E_{\text{system}} + E_{\text{surrounding}} = \text{constant}$$

First Law of Thermodynamics

$$E(\text{system}) + E(\text{surrounding}) = \text{constant}$$

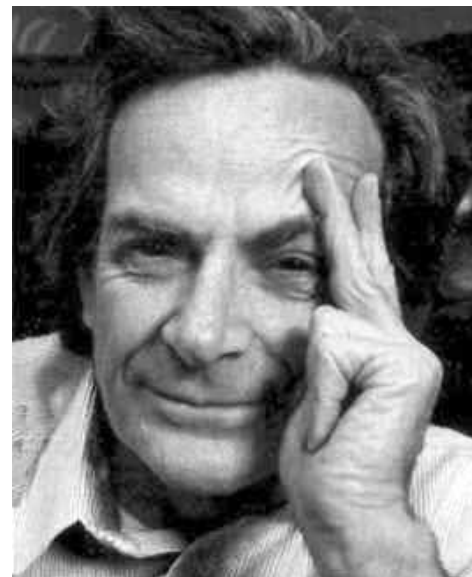


$$E = mc^2$$

First Law of Thermodynamics

$$E(\text{system}) + E(\text{surrounding}) = \text{constant}$$

Energy is an abstract thing, we don't know exactly what energy is !



State Variables

- State variables:
 P, V, T , etc.

Experimental observables

- State functions:

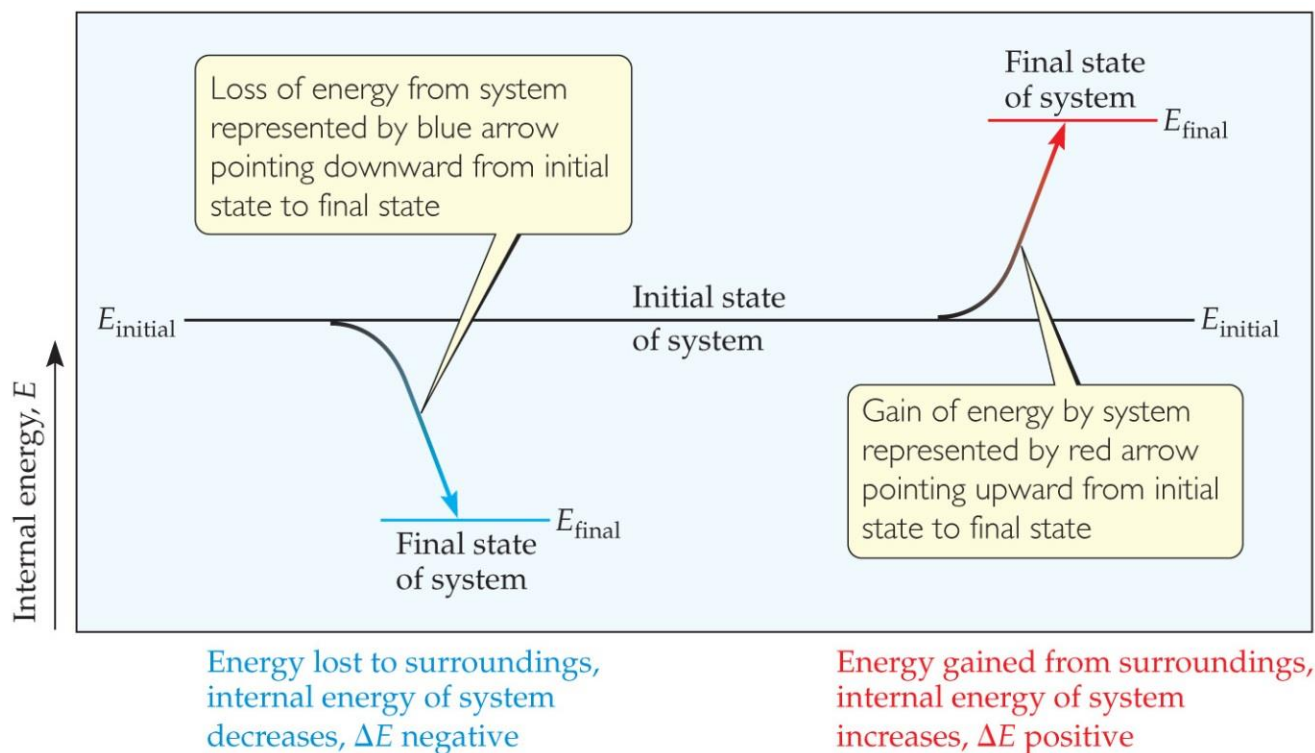
function
↓
 $f(x, y)$
↗ ↘
variables

$$E = \frac{3}{2} RT$$

Energy of monatomic ideal gas

Internal Energy

The **internal energy** of a system is the sum of all kinetic and potential energies of all components of the system; we call it E .



Internal Energy

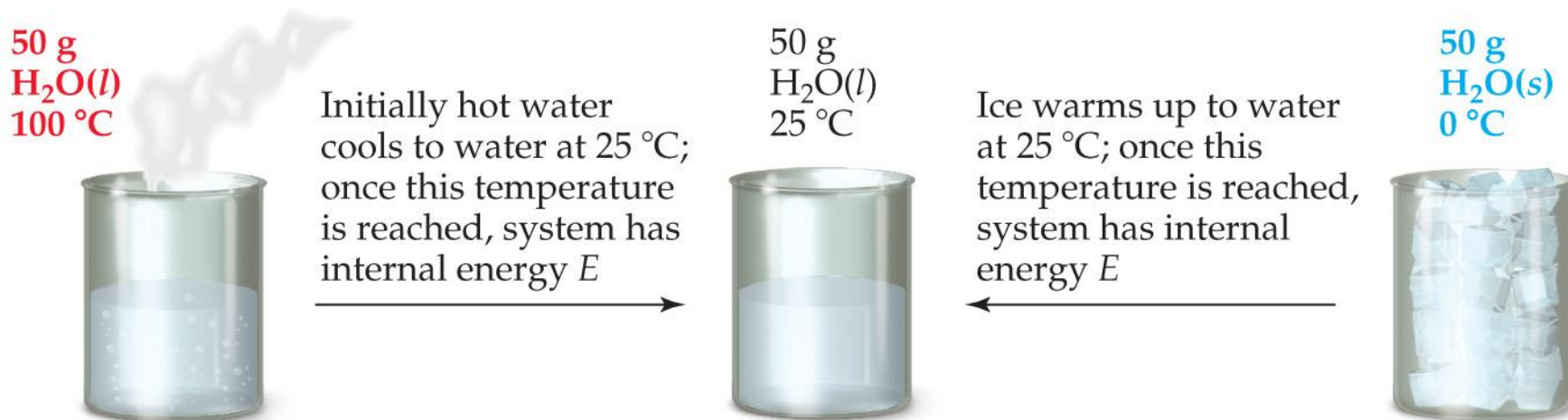
Usually we have no way of knowing the internal energy of a system in condensed phase; finding that value is simply too complex a problem.

50 g
 $\text{H}_2\text{O}(l)$
 25°C



Internal Energy

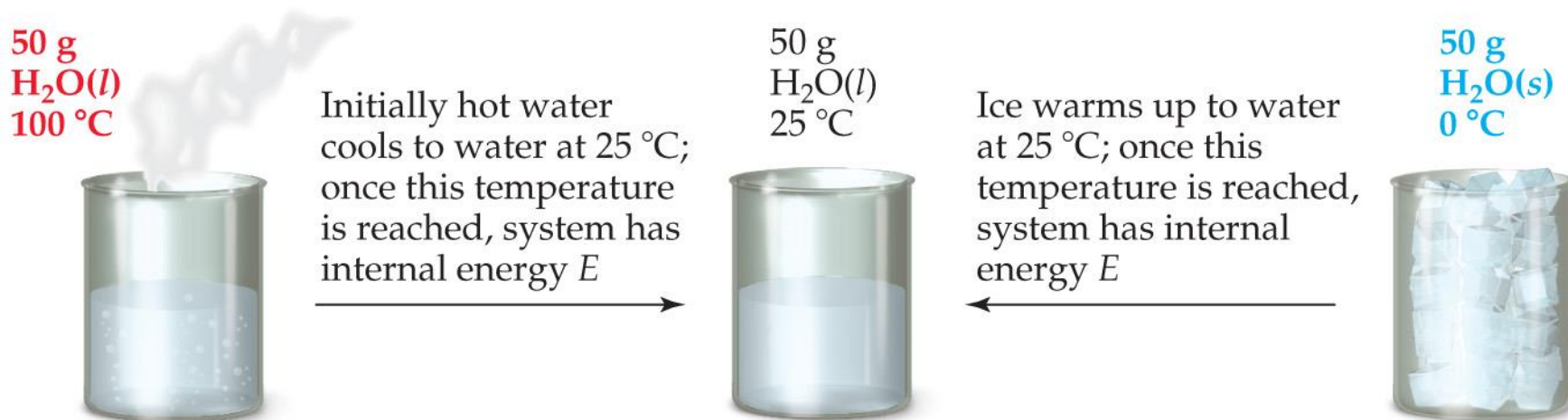
- However, we do know that the internal energy of a system is independent of the path by which the system achieved that state.
 - In the system depicted in the following figure, the water could have reached room temperature from either direction.



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Internal Energy

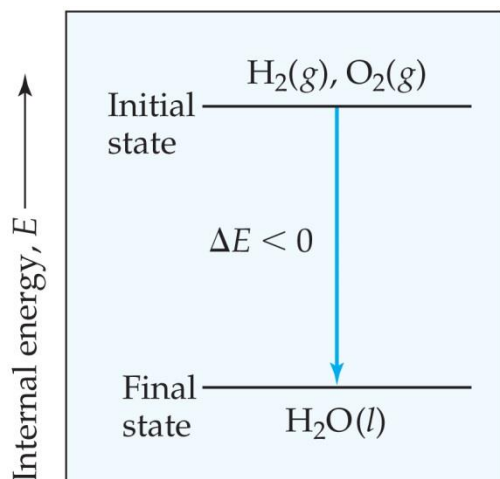
- Therefore, internal energy is a state function.
- It depends only on the present state of the system, not on the path by which the system arrived at that state.
- And so, ΔE depends only on E_{initial} and E_{final} .



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First Law of Thermodynamics

By definition, the change in internal energy, ΔE , is the final energy of the system minus the initial energy of the system: $\Delta E = E_{\text{final}} - E_{\text{initial}}$



E_{initial} greater than E_{final} , energy released from system to surroundings during reaction, $\Delta E < 0$

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- When energy is exchanged between the system and the surroundings, it is exchanged as either heat (q) or work (w).

$$\Delta E = q + w$$

ΔE , q , w , and Their Signs

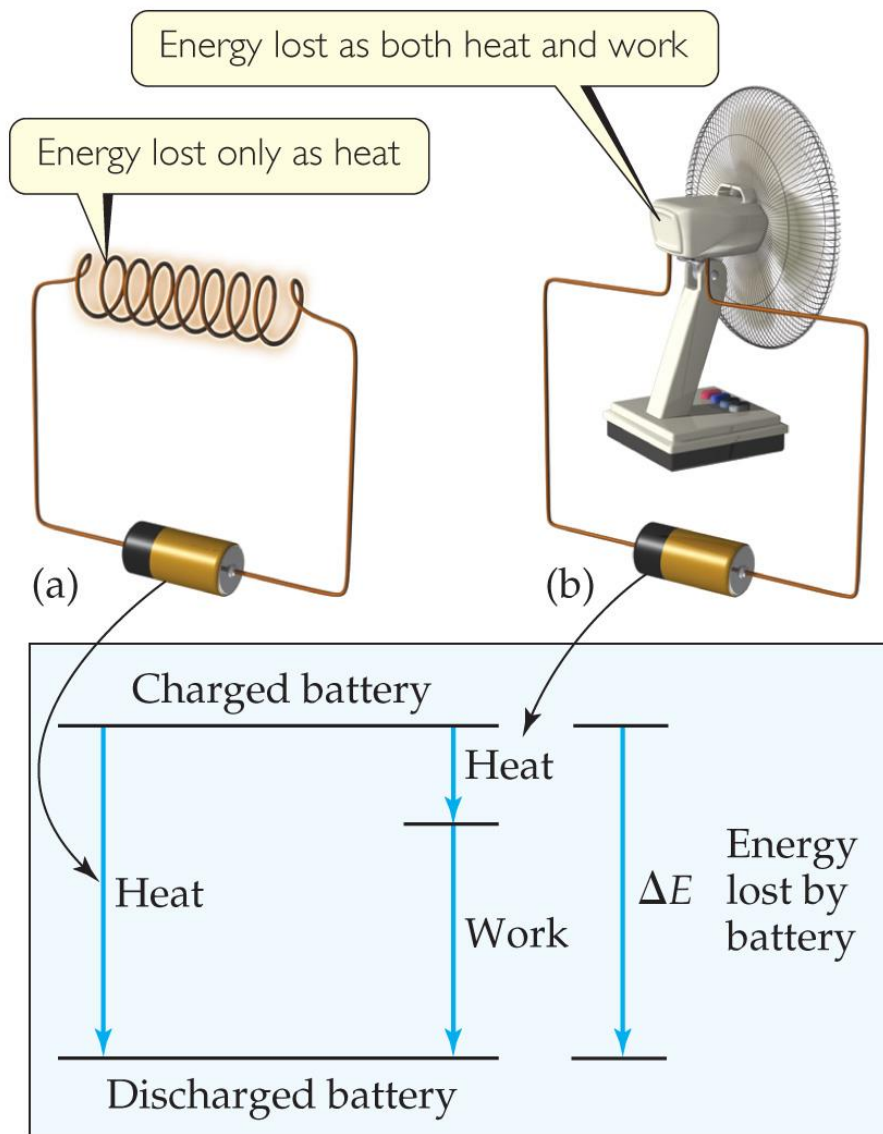
TABLE 5.1 • Sign Conventions for q , w , and ΔE

For q	+ means system <i>gains</i> heat	– means system <i>loses</i> heat
For w	+ means work done <i>on</i> system	– means work done <i>by</i> system
For ΔE	+ means <i>net gain</i> of energy by system	– means <i>net loss</i> of energy by system

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From the system's point of view

Heat and Work Are Not State Functions



- By definition, q and w are *not* state functions.
- Whether the battery is shorted out or is discharged by running the fan, its ΔE is the same.
 - But q and w are different in the two cases.

State Functions and Path Functions

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



Potential energy of **hiker 1** and **hiker 2** is the same although they took different paths.

- ▶ Work (w) and heat (q) are **path functions**. They depend on the path to achieve that condition.

Potential energy (U), pressure (P), volume (V), and temperature (T) are state functions.

$$\Delta U = U_{\text{final}} - U_{\text{initial}}$$

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

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

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

Enthalpy

- For most chemical reactions, we only need to consider the work done due to volume expansion or contraction, i.e. $w = -P_{\text{ext}} \Delta V$
- Under the condition of constant system pressure, we have

$$w = -P_{\text{ext}} \Delta V = -P_{\text{sys}} \Delta V \equiv -P \Delta V$$

- First law of thermodynamics
 - $\Delta E = q + w = q_P - P \Delta V$
 - $q_P = \Delta E + P \Delta V = \Delta E + \Delta(PV) = \Delta(E + PV)$

Enthalpy

$$q_P = \Delta(E + PV)$$

The heat change under constant pressure is independent of path!

- **Enthalpy** is defined as the internal energy plus the product of pressure and volume:

$$H = E + PV$$

At constant **system** pressure, ΔH is the heat gained or lost of the system.

Enthalpy

- If a process takes place **at constant pressure** (as the majority of processes we study do) and the only work done is this **pressure–volume work**, we can account for **heat flow** during the process by measuring the **enthalpy** of the system.
- **Enthalpy** is the internal energy plus the product of pressure and volume:

$$H = E + PV$$

Enthalpy

- When the system changes at constant pressure, the change in enthalpy, ΔH , is

$$\Delta H = \Delta(E + PV)$$

- This can be written

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

Enthalpy

- Since $\Delta E = q + w$ and $w = -P\Delta V$, we can substitute these into the enthalpy expression:

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

$$\Delta H = (q + w) - w$$

$$\Delta H = q$$

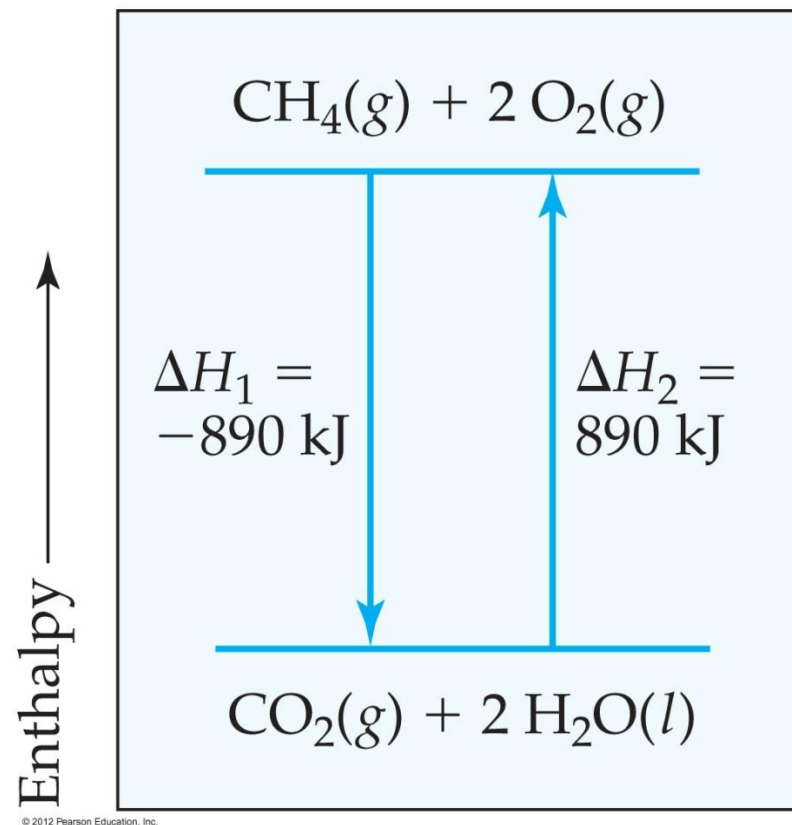
- So, at constant pressure, the **change in enthalpy** is the **heat gained or lost**.

$$\Delta H = q_p$$

Enthalpy of Reaction

The *change* in enthalpy, ΔH , is the enthalpy of the products minus the enthalpy of the reactants:

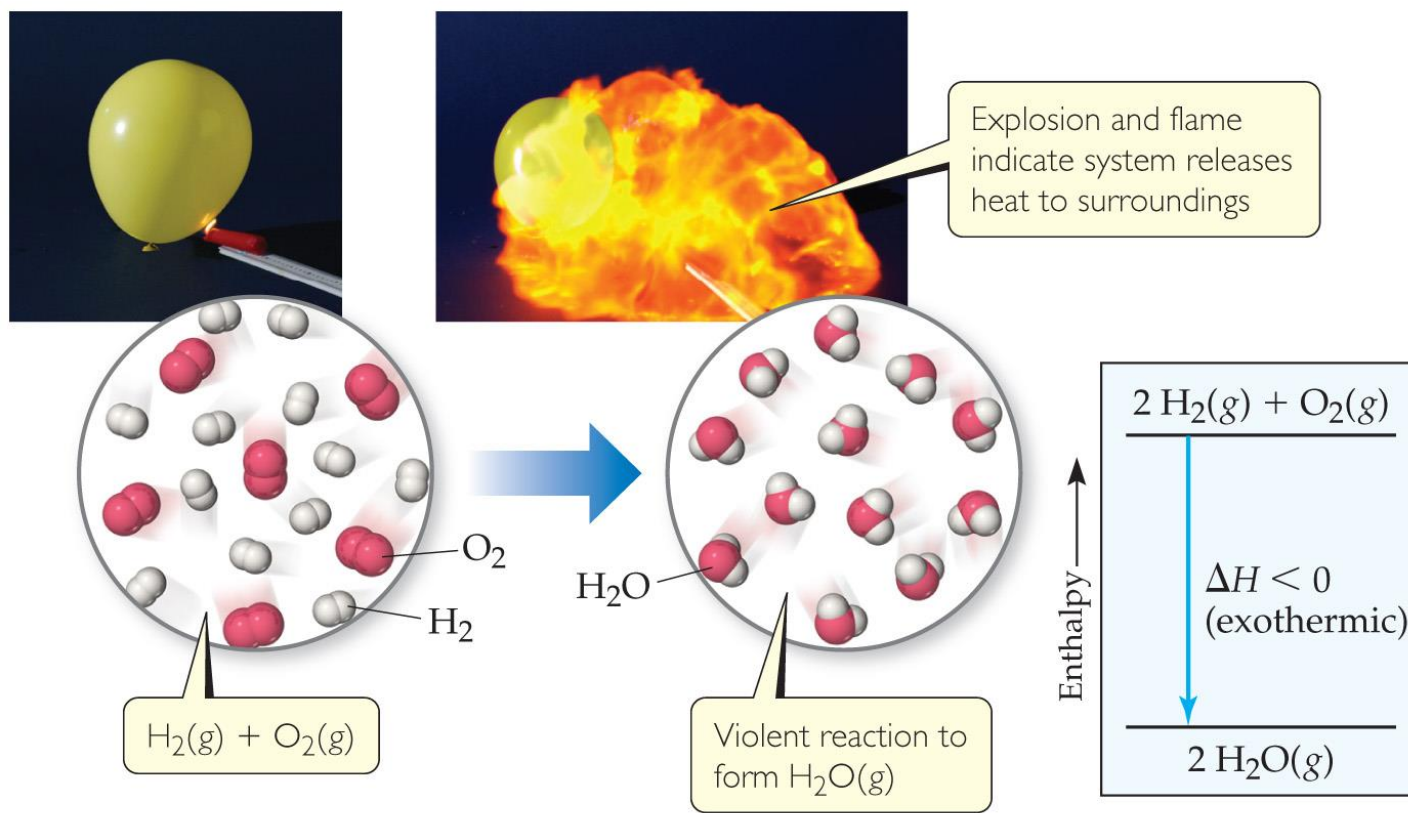
$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$



$\Delta H < 0$, exothermic; $\Delta H > 0$, endothermic

Enthalpy of Reaction

This quantity, ΔH , is called the **enthalpy of reaction**, or the **heat of reaction**.



More about Enthalpy

- Enthalpy is an extensive property.

Enthalpy of reaction (Heat of combustion)

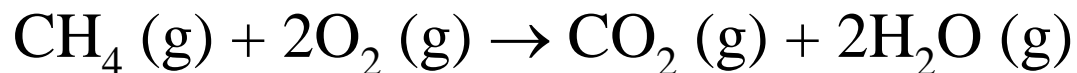


Don't forget to specify the amount because
enthalpy is an extensive property.

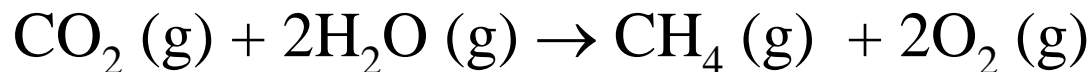


More about Enthalpy

- ΔH for a reaction in the forward direction is equal in size, but opposite in sign, to ΔH for the reverse reaction.



$$\Delta H = -191.3 \text{ kcal/mol}$$



$$\Delta H = 191.3 \text{ kcal/mol}$$

More about Enthalpy

- ΔH for a reaction depends on the state of the products and the state of the reactants.

At different T and P , ΔH will be different!

Standard conditions:

1 atm, 1 M,
temperature of interest (usually 298 K)

Heat Capacity and Specific Heat

- The amount of energy required to raise the temperature of a substance by 1 K (1°C) is its **heat capacity**.
- If the heat capacity is given *per gram* of substance, it is called **specific heat** with the unit of $\text{J K}^{-1} \text{g}^{-1}$ or $\text{J } ^\circ\text{C}^{-1} \text{g}^{-1}$. It is the energy required to raise the temperature of 1 g of a substance by 1°C.
- If the heat capacity is given *per mole* of the substance, it is called **molar heat capacity**. It has the unit of $\text{J K}^{-1} \text{mol}^{-1}$ or $\text{J } ^\circ\text{C}^{-1} \text{mol}^{-1}$.

TABLE 5.2 • Specific Heats of Some Substances at 298 K

Elements		Compounds	
Substance	Specific Heat (J/g-K)	Substance	Specific Heat (J/g-K)
$\text{N}_2(\text{g})$	1.04	$\text{H}_2\text{O}(\text{l})$	4.18
$\text{Al}(\text{s})$	0.90	$\text{CH}_4(\text{g})$	2.20
$\text{Fe}(\text{s})$	0.45	$\text{CO}_2(\text{g})$	0.84
$\text{Hg}(\text{l})$	0.14	$\text{CaCO}_3(\text{s})$	0.82

Heat Capacity

- For an ideal gas,

$$(\text{KE})_{\text{avg}} = \frac{3}{2}RT$$

- Energy required to change the energy of 1 mole of an ideal gas by ΔT is

$$\text{Energy ("heat")} \text{ required} = \frac{3}{2}R\Delta T$$

- The **molar heat capacity** of a substance is defined as the energy required to raise the temperature of 1 mole of that substance by 1 K. Thus we may conclude that the molar heat capacity of an ideal gas is $\frac{3}{2} R$.

Heat Capacity

- Heating an Ideal Gas at Constant Volume

$$C_v = \frac{3}{2}R = \text{“heat” required to change the temperature of 1 mol of gas by 1 K at constant volume}$$

- Heating an Ideal Gas at Constant Pressure

$$\text{Energy required} = \text{“heat”} = \begin{array}{c} \text{energy needed} \\ \text{to change the} \\ \text{translational energy} \end{array} + \begin{array}{c} \text{energy needed to} \\ \text{do the } PV \text{ work} \end{array}$$

$$P\Delta V = nR\Delta T = R\Delta T \quad (\text{per mole})$$

$$\text{Heat required to increase the temperature of 1 mol of gas by 1 K (constant } P) = \frac{3}{2}R + R = \frac{5}{2}R$$

$$= C_v + R = C_p$$

Heat Capacity

- Heating a Gas: Energy and Enthalpy

$$E = \frac{3}{2}RT \quad (\text{per mole})$$

$$\Delta E = \frac{3}{2}R\Delta T \quad (\text{per mole})$$

$$\Delta E = C_v\Delta T \quad (\text{per mole})$$

$$\Delta E = nC_v\Delta T \quad (n \text{ moles})$$

$$\begin{aligned} \text{“Heat” required} &= q_p = nC_p\Delta T \\ &= n(C_v + R)\Delta T \\ &= \underbrace{nC_v\Delta T}_{\Delta E} + \underbrace{nR\Delta T}_{P\Delta V = \text{work required}} \end{aligned}$$

Heat Capacity

$$H = E + PV$$

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta H = \Delta E + \Delta(nRT) = \Delta E + nR\Delta T$$

$$\Delta H = nC_v\Delta T + nR\Delta T$$

$$= n(C_v + R)\Delta T = nC_p\Delta T$$

$$E \propto T \quad \text{and} \quad H \propto T$$

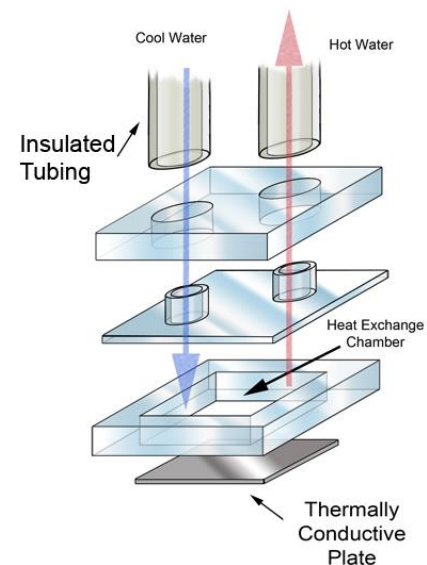
$$q = nC\Delta T$$

Heat Capacity

Thermodynamic Properties of an Ideal Gas

Expression	Application
$C_v = \frac{3}{2}R$	Monatomic ideal gas
$C_v > \frac{3}{2}R$	Polyatomic ideal gas (value must be measured experimentally)
$C_p = C_v + R$	All ideal gases
$C_p = \frac{5}{2}R = \frac{3}{2}R + R$	Monatomic ideal gas
$C_p > \frac{5}{2}R$	Polyatomic ideal gas (specific value depends on the value of C_v)
$\Delta E = nC_v\Delta T$	All ideal gases
$\Delta H = nC_p\Delta T$	All ideal gases

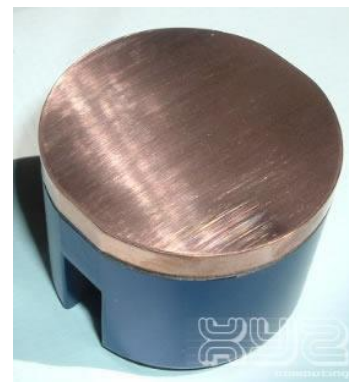
Heat Capacity and Specific Heat



Liquid N₂



Iced water

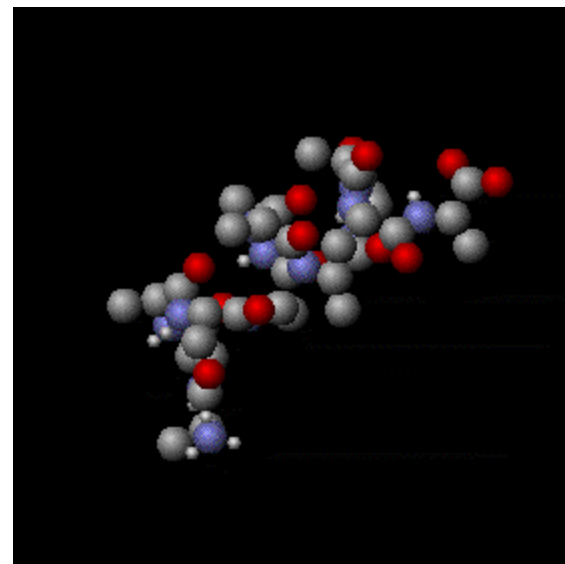


Metal block with
water cooling

Microscopic Origin of Heat Capacity

Energy can be absorbed by a substance in various forms:

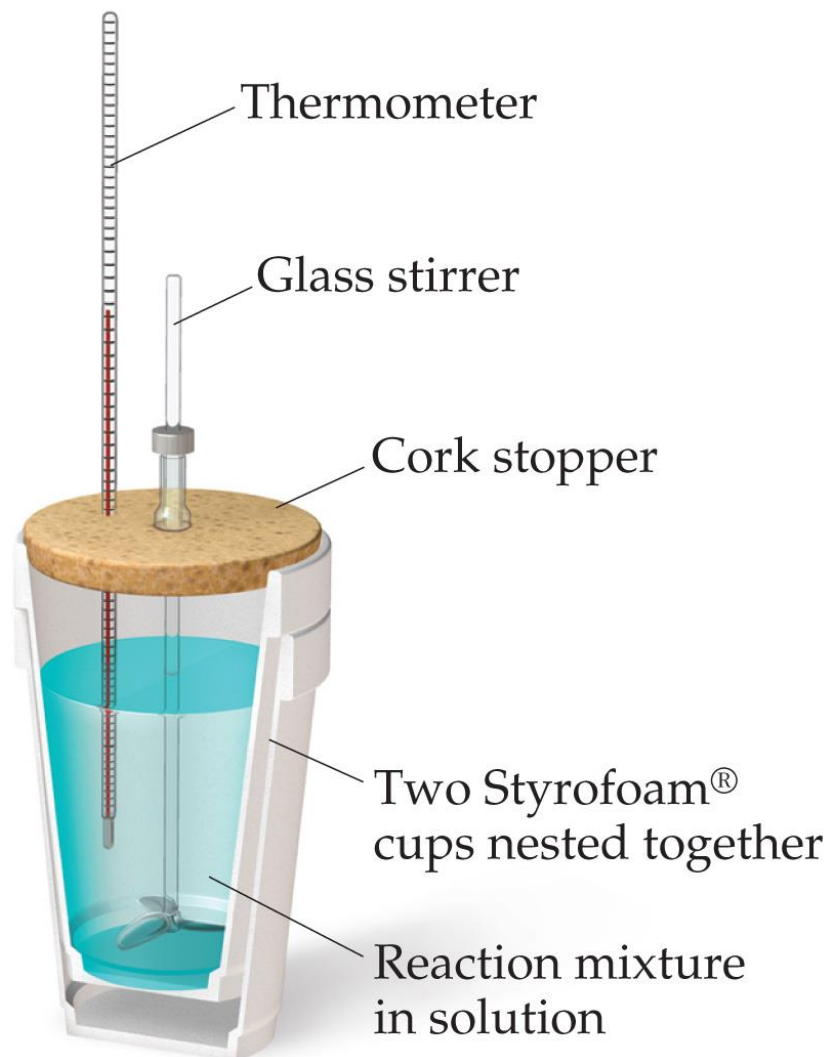
1. Translational kinetic energy
2. Vibrational energy
3. Rotational energy
4. Intermolecular bonding breaking



For most situations, translational kinetic energy is directly proportional to temperature.

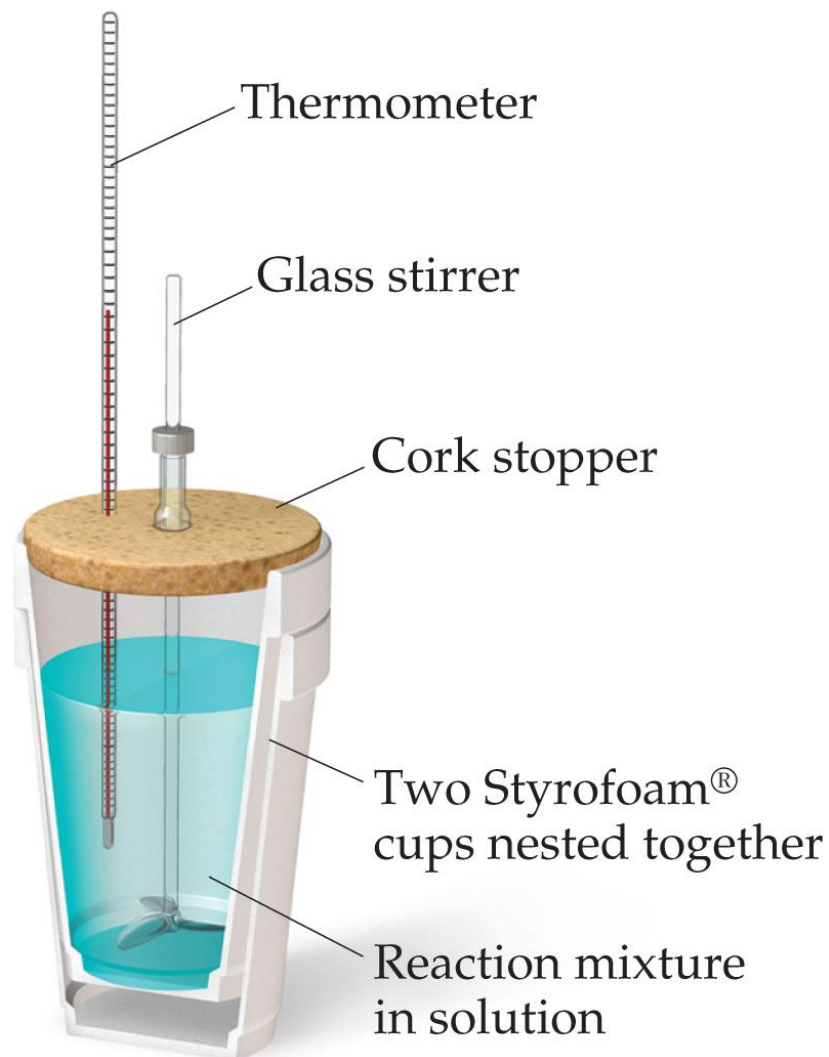
The more the forms (degree of freedom), the larger the heat capacity.

Constant Pressure Calorimetry



By carrying out a reaction in aqueous solution in a simple calorimeter such as this one, one can indirectly measure the heat change for the system by measuring the heat change for the water in the calorimeter.

Constant Pressure Calorimetry

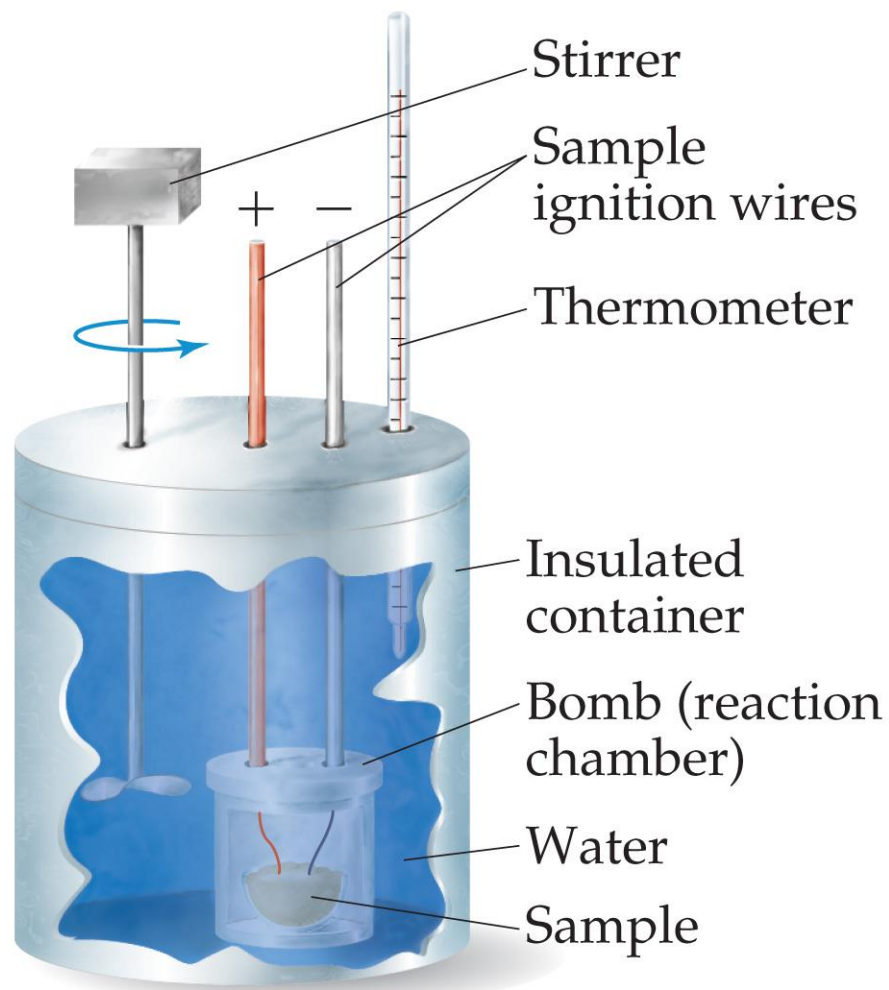


Because the specific heat for water is well known ($4.184 \text{ J/g}\cdot\text{K}$), we can measure ΔH for the reaction with this equation:

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

Bomb Calorimetry

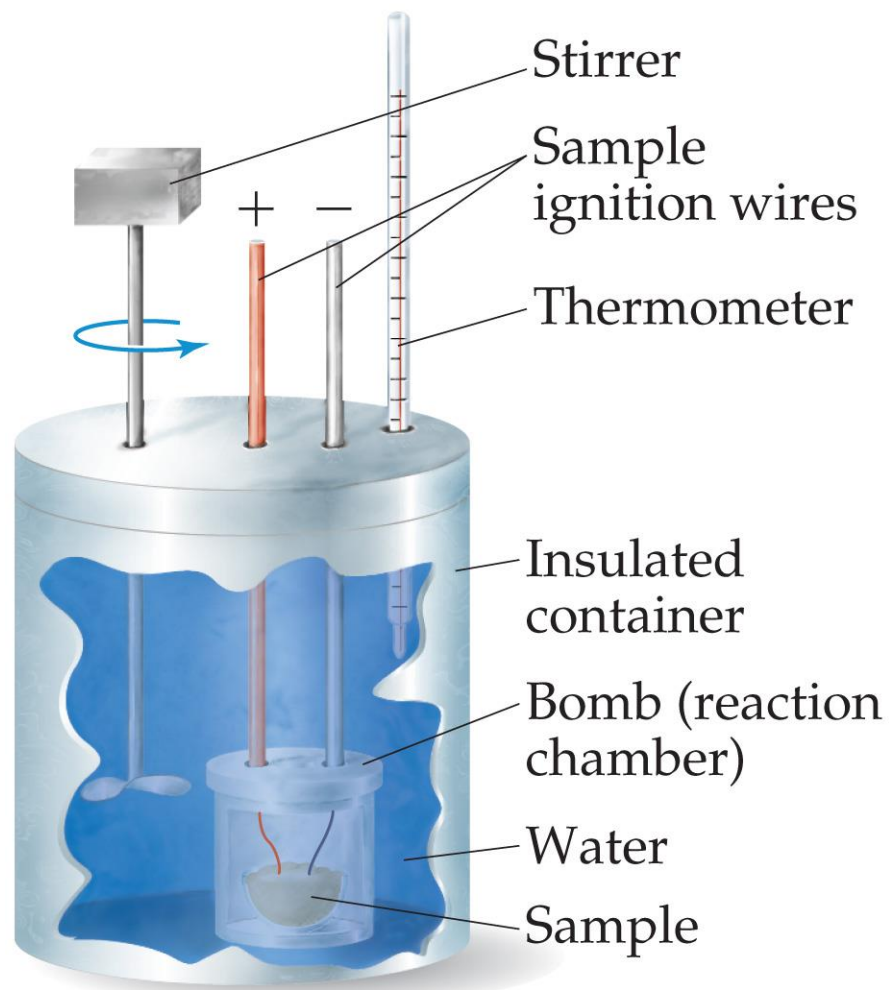
- Reactions can be carried out in a sealed “bomb” such as this one.
- The heat absorbed (or released) by the water is a very good approximation of the enthalpy change for the reaction.



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Bomb Calorimetry

- Because the volume in the bomb calorimeter is constant, what is measured is really the change in internal energy, ΔE , not ΔH .
- For most reactions, the difference is very small.



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Hess's Law

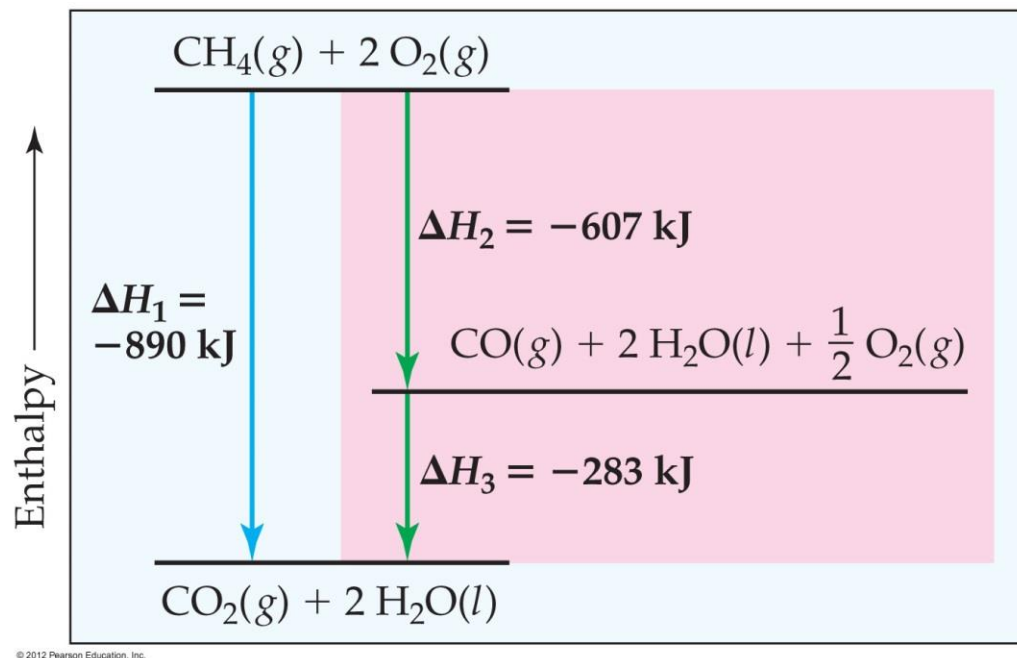
Which one is more important, process or result?



Process doesn't matter!
Only the starting and finishing
conditions are important!

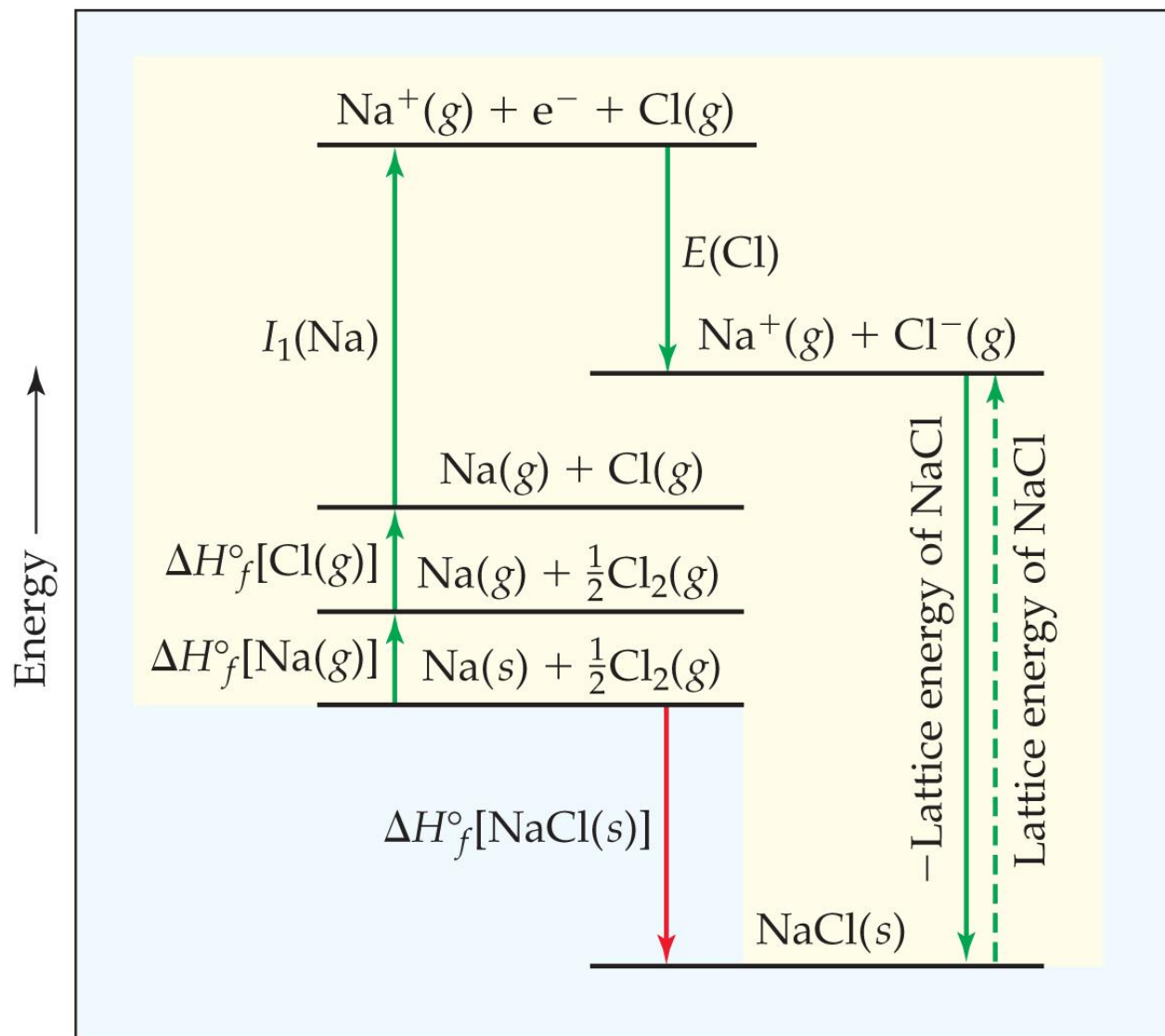
Any process carried out in several steps, the overall ΔH is equal to the sum of the enthalpy changes (signed) for the individual steps.

Hess's Law



Because ΔH is a state function, the total enthalpy change depends only on the initial state of the reactants and the final state of the products.

Formation of an Ionic Solid



Enthalpies of Formation

Standard heat of formation, ΔH_f^0

Elements at standard states \rightarrow Compound at standard states

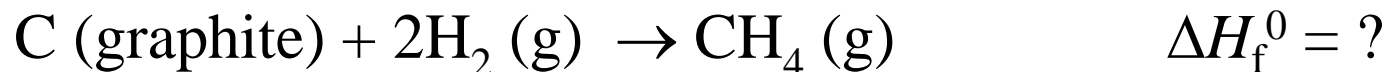
Standard states are the thermodynamically most stable form of a substance at the particular temperature of interest at 1 atm

Carbon — graphite

Oxygen — O_2 (g)

Water — H_2O (l)

ΔH of Formation

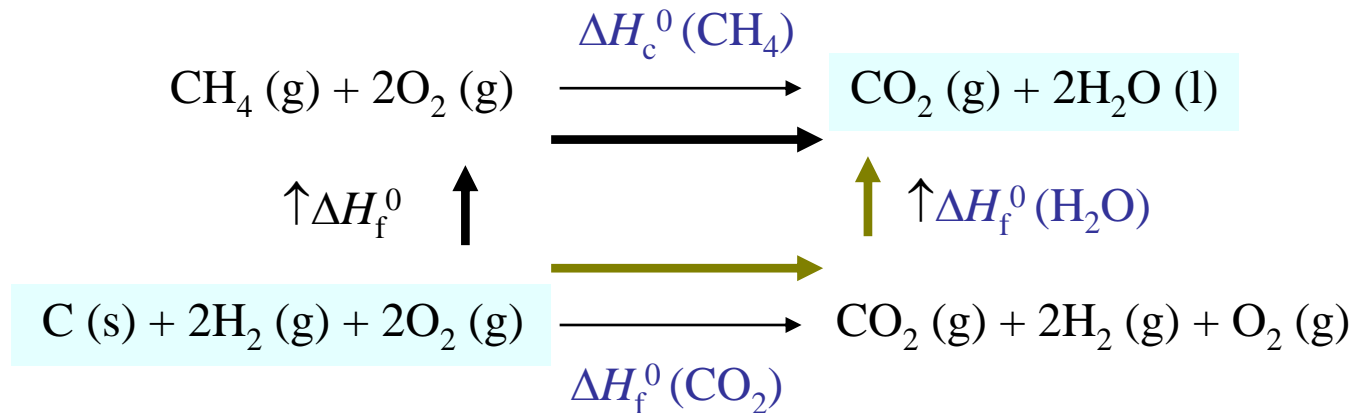


$$\Delta H_{\text{f}}^0 (\text{CO}_2) = -93.963 \text{ kcal/mol}$$

$$\Delta H_{\text{f}}^0 (\text{H}_2\text{O}) = -68.317 \text{ kcal/mol}$$

$$\Delta H_{\text{c}}^0 (\text{CH}_4) = -210.8 \text{ kcal/mol}$$

ΔH of Formation



$$\Delta H_f^0(\text{CO}_2) = -93.963 \text{ kcal/mol}$$

$$\Delta H_f^0(\text{H}_2\text{O}) = -68.317 \text{ kcal/mol}$$

$$\Delta H_c^0(\text{CH}_4) = -210.8 \text{ kcal/mol}$$

$$\Delta H_f^0 + (-210.8) = (-93.963) + (-68.317) \times 2$$

Hess' Law:

$$\begin{aligned}
 \Delta H_f^0(\text{CH}_4) &= 210.8 - 93.963 + 2 \times (-68.317) \\
 &= -19.797 \text{ kcal/mol} \\
 &= -19.8 \text{ kcal/mol}
 \end{aligned}$$

ΔH of Formation

$$\Delta H_{\text{reaction}}^0 = \sum \Delta H_f^0 (\text{products}) - \sum \Delta H_f^0 (\text{reactants})$$

$$\Delta H_f^0 (\text{elements}) = 0$$

$$\Delta H_f^0 (\text{diamond}) \neq 0$$



+1.88 kJ/mol ?



−1.88 kJ/mol ?

Standard Enthalpies of Formation

Standard enthalpies of formation, ΔH_f° , are measured under standard conditions (1 atm) and typically 25°C.

TABLE 5.3 • Standard Enthalpies of Formation, ΔH_f° , at 298 K

Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$\text{C}_2\text{H}_2(\text{g})$	226.7	Hydrogen chloride	$\text{HCl}(\text{g})$	-92.30
Ammonia	$\text{NH}_3(\text{g})$	-46.19	Hydrogen fluoride	$\text{HF}(\text{g})$	-268.60
Benzene	$\text{C}_6\text{H}_6(\text{l})$	49.0	Hydrogen iodide	$\text{HI}(\text{g})$	25.9
Calcium carbonate	$\text{CaCO}_3(\text{s})$	-1207.1	Methane	$\text{CH}_4(\text{g})$	-74.80
Calcium oxide	$\text{CaO}(\text{s})$	-635.5	Methanol	$\text{CH}_3\text{OH}(\text{l})$	-238.6
Carbon dioxide	$\text{CO}_2(\text{g})$	-393.5	Propane	$\text{C}_3\text{H}_8(\text{g})$	-103.85
Carbon monoxide	$\text{CO}(\text{g})$	-110.5	Silver chloride	$\text{AgCl}(\text{s})$	-127.0
Diamond	$\text{C}(\text{s})$	1.88	Sodium bicarbonate	$\text{NaHCO}_3(\text{s})$	-947.7
Ethane	$\text{C}_2\text{H}_6(\text{g})$	-84.68	Sodium carbonate	$\text{Na}_2\text{CO}_3(\text{s})$	-1130.9
Ethanol	$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-277.7	Sodium chloride	$\text{NaCl}(\text{s})$	-410.9
Ethylene	$\text{C}_2\text{H}_4(\text{g})$	52.30	Sucrose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$	-2221
Glucose	$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	-1273	Water	$\text{H}_2\text{O}(\text{l})$	-285.8
Hydrogen bromide	$\text{HBr}(\text{g})$	-36.23	Water vapor	$\text{H}_2\text{O}(\text{g})$	-241.8

Energy in Foods

Most of the fuel in the food we eat comes from carbohydrates and fats.

TABLE 5.4 • Compositions and Fuel Values of Some Common Foods

	Approximate Composition (% by mass)			Fuel Value	
	Carbohydrate	Fat	Protein	kJ/g	kcal/g (Cal/g)
Carbohydrate	100	—	—	17	4
Fat	—	100	—	38	9
Protein	—	—	100	17	4
Apples	13	0.5	0.4	2.5	0.59
Beer [†]	1.2	—	0.3	1.8	0.42
Bread	52	3	9	12	2.8
Cheese	4	37	28	20	4.7
Eggs	0.7	10	13	6.0	1.4
Fudge	81	11	2	18	4.4
Green beans	7.0	—	1.9	1.5	0.38
Hamburger	—	30	22	15	3.6
Milk (whole)	5.0	4.0	3.3	3.0	0.74
Peanuts	22	39	26	23	5.5

[†]Beer typically contains 3.5% ethanol, which has fuel value.

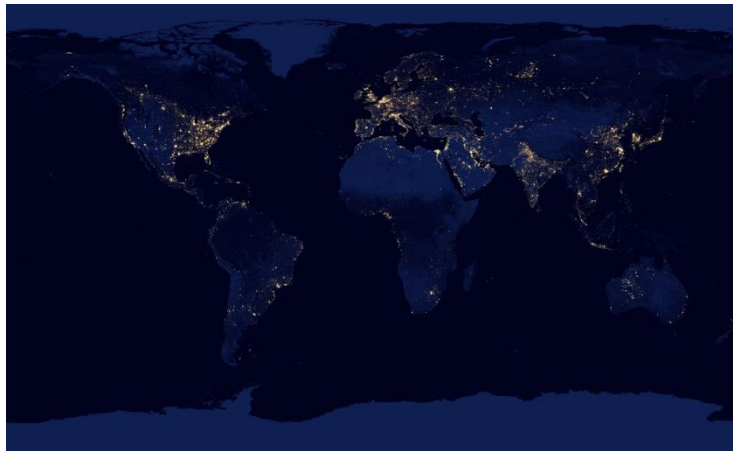
*Although fuel values represent the heat *released* in a combustion reaction, fuel values are reported as positive numbers.

Fuels

Current worldwide energy consumption rate :

$\sim 15 \text{ TW}$ (1 W = 1 J/s)

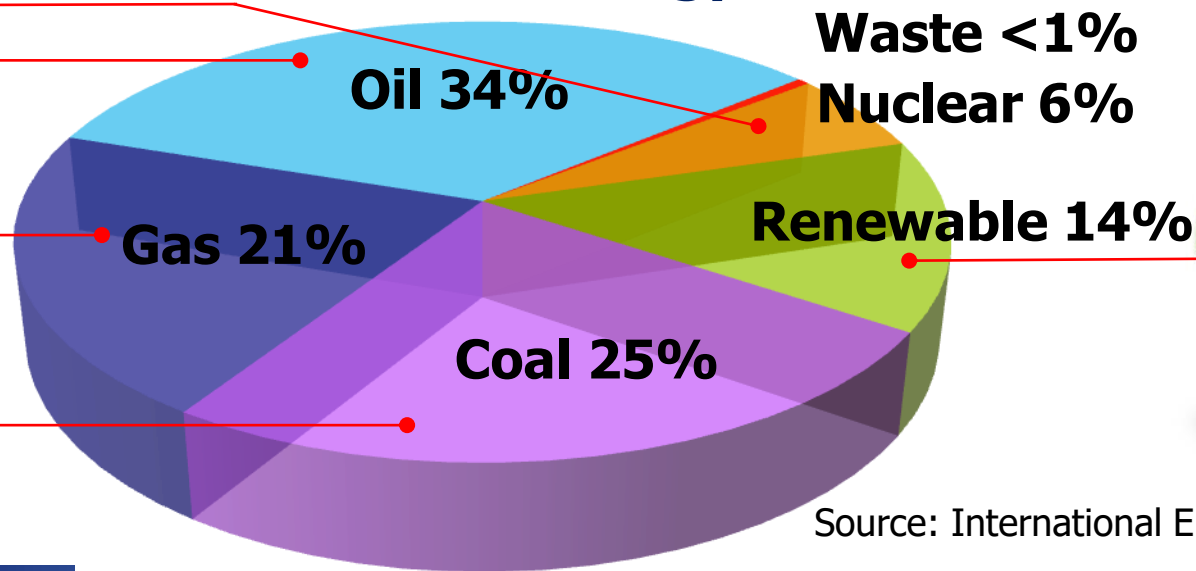
Ref: R. E. Blankenship et al. *Science* 2011, 332, 805



NASA Earth Observatory image by Robert Simmon (took in 2012)

Possible options for meeting the 15 TW-Challenge

Current worldwide energy sources



Source: International Energy Agency (IEA)

Fossil fuel

Oil price is rapidly increasing, many kind of undesired pollutions are produced (air, water, green house).

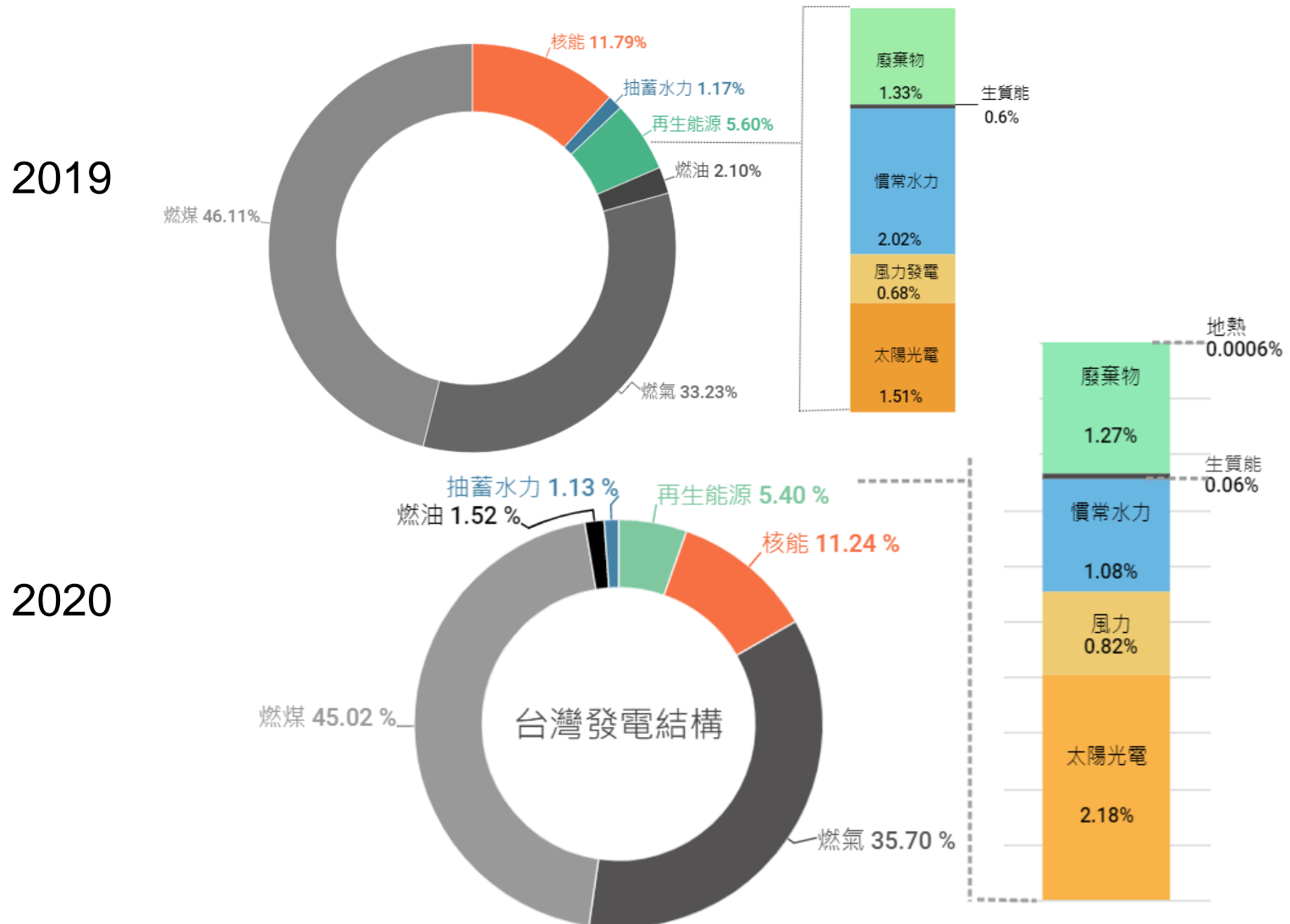


Nuclear power

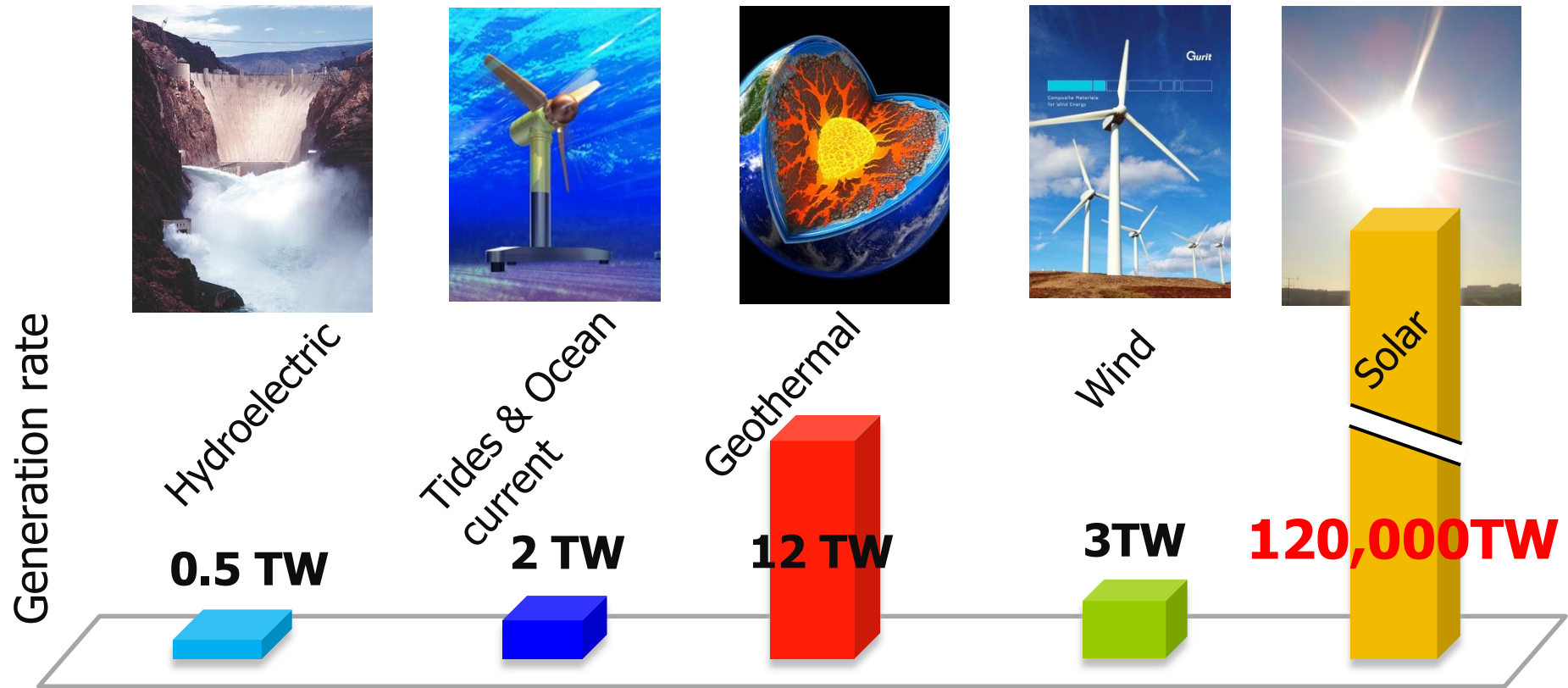
There are now over 430 commercial nuclear power reactors operating in 31 countries, with 0.4 TW of total capacity.



Sources of Energy in Taiwan



Renewable Energy Sources



If 1 day of solar irradiation is captured to generate energy (assume 5% efficiency), how long will it support the energy we are consuming ?

$$\text{Ans: } \frac{1.2 \times 10^5 \text{ TW} \times 5\% \times 1 \text{ day}}{15 \text{ TW} \times 1 \text{ day}} = 400 \text{ (day)} = \mathbf{1.1 \text{ year !!}}$$