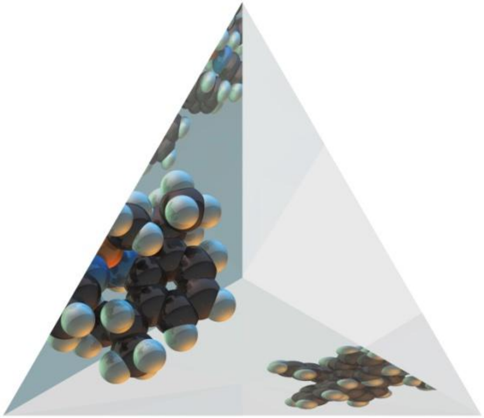


CHEMISTRY

The Central Science

8th Edition

Chapter 5
Thermochemistry

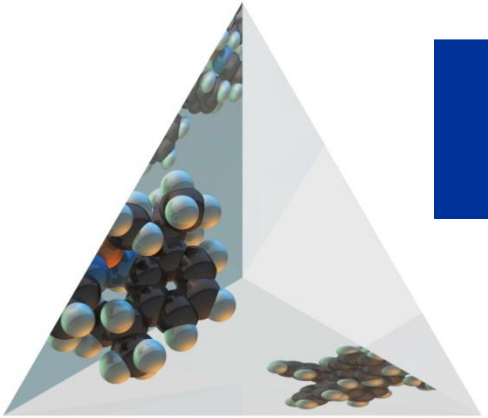
Dr. Kozet YAPSAKLI

What is Energy?

- Energy is the ***capacity to do work or to transfer heat***

-**Kinetic Energy**: energy associated with mass in motion (recall: $E_k = \frac{1}{2}mv^2$)

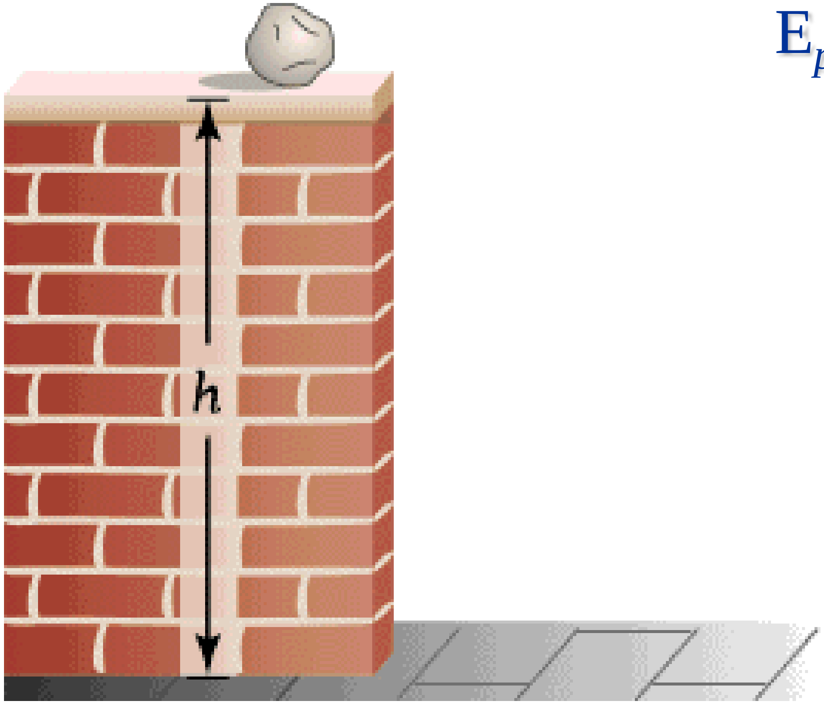
-**Potential Energy:** energy associated with the *position* of an object relative to other objects (energy that is *stored* - can be converted to kinetic energy)



The Nature of Energy

Kinetic and Potential Energy

- Potential energy can be converted into kinetic energy.



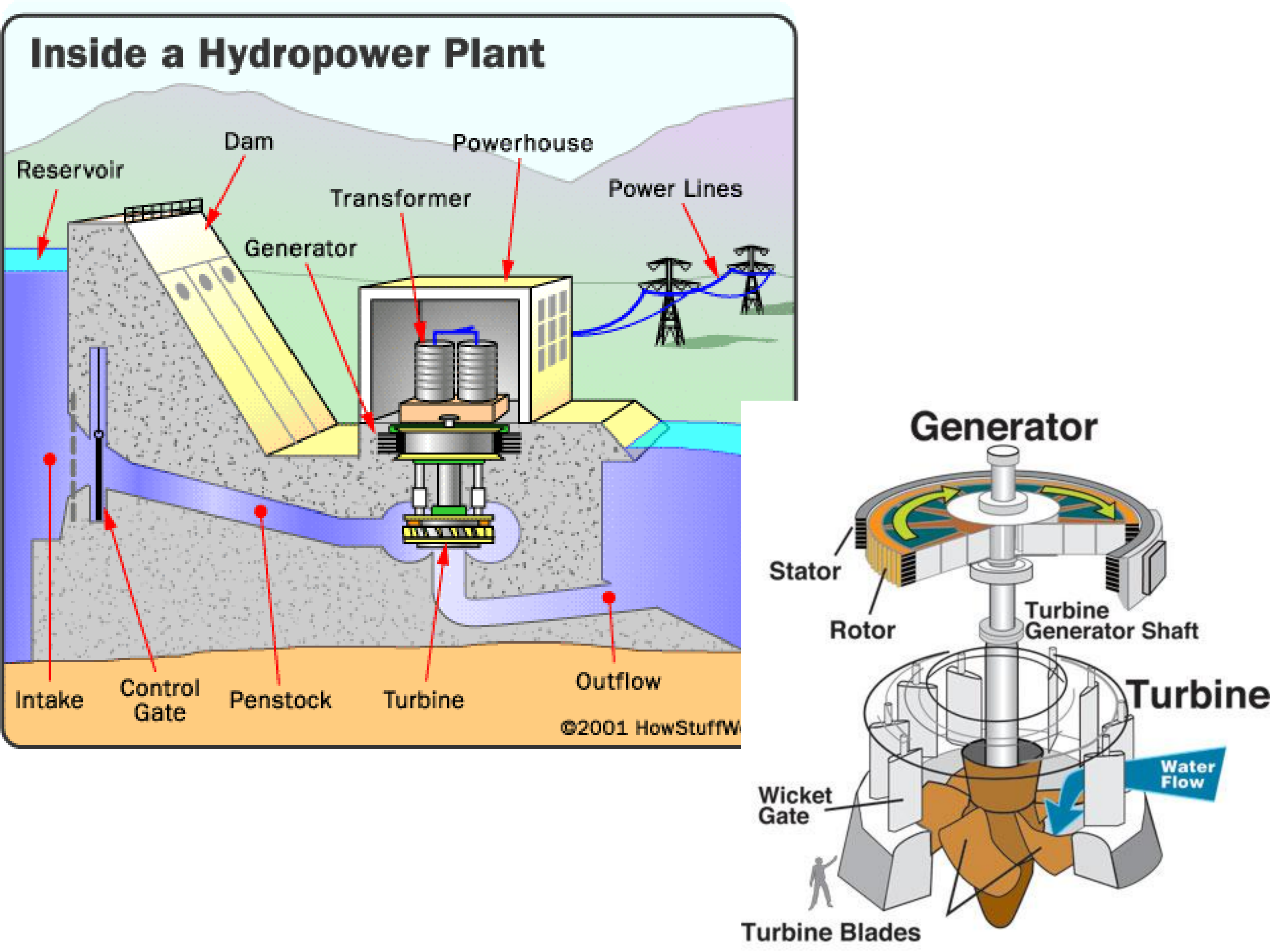
$E_p = mgh$

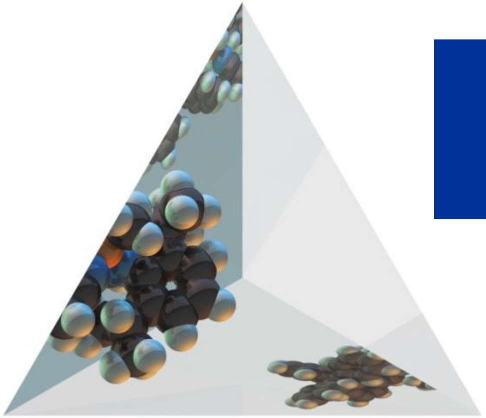
$$E_k = \frac{1}{2}mv^2$$

E_k increases as velocity increases and mass increases.

As the ball falls, it is potential energy is converted to kinetic energy.

Potential energy can be converted into kinetic energy.


Inside a Hydropower Plant
Reservoir
Dam
Powerhouse
Transformer
Power Lines
Generator
Intake
Control Gate
Penstock
Turbine
Outflow
©2001 HowStuffW
Generator
Stator
Rotor
Turbine Generator Shaft
Turbine
Water Flow
Wicket Gate
Turbine Blades



The Nature of Energy

Units of Energy

- SI Unit for energy is the joule, J:

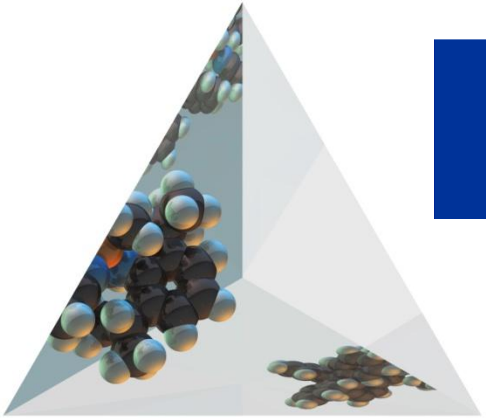
$$E_k = \frac{1}{2}mv^2 = \frac{1}{2}(2\ \mathrm{kg})(1\ \mathrm{m/s})^2$$

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

We sometimes use the calorie instead of the joule:

1 cal = 4.184 J (exactly)

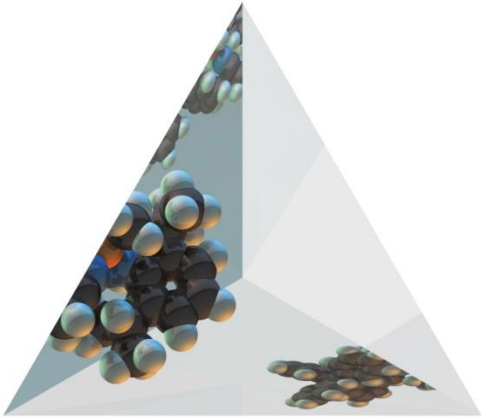
1 Cal = 1000 cal = 1 kcal

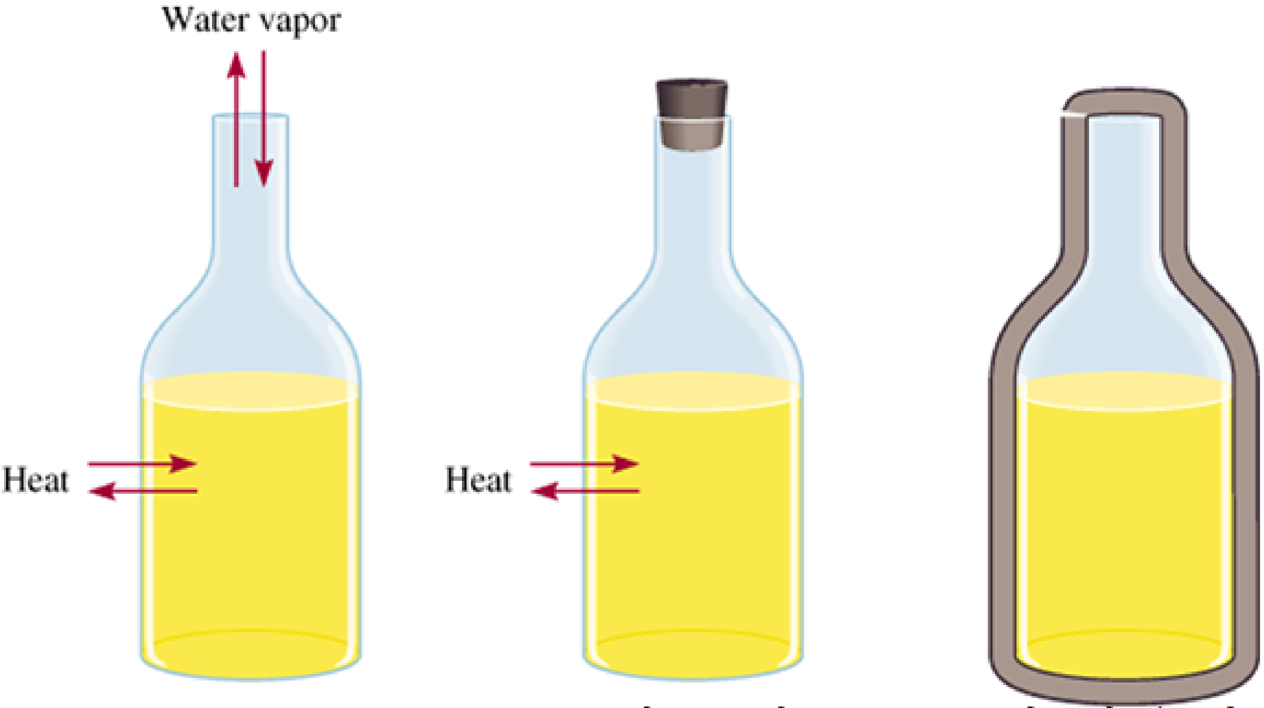


The Nature of Energy

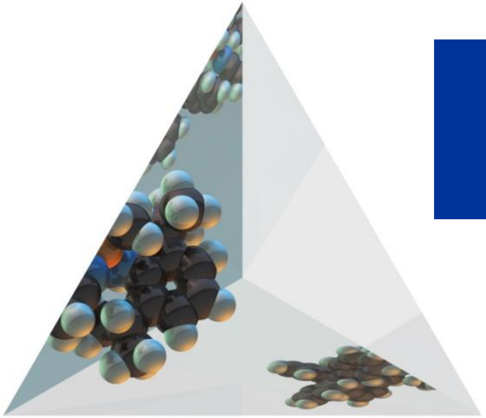
Systems and Surroundings

- System: part of the universe we are interested in.
- Surroundings: the rest of the universe.





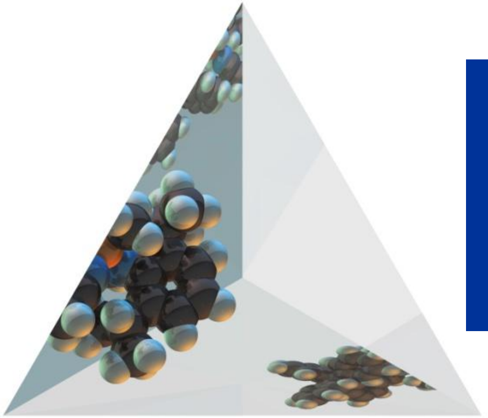
	open	closed	isolated
Exchange:	mass & energy	energy	nothing



The Nature of Energy

Transferring Energy: Work and Heat

- Work is the product of force applied to an object over a distance:
- Heat is the transfer of energy between two objects.



The First Law of Thermodynamics

Energy is neither created nor destroyed

- Energy of (system + surroundings) is constant.
- Any energy transferred from a system must be transferred to the surroundings (and *vice versa*).
- Internal Energy: total energy of a system.
- Change in internal energy,

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

First Law of Thermodynamics

- "The total energy of the universe is *constant*."
- "Energy is neither created or destroyed in a process, only converted to another form."

  -Conservation of Energy
- "*You can't win . . . you can only break even.*"

$$\boxed{\Delta E = q + w}$$

Change in energy of the system

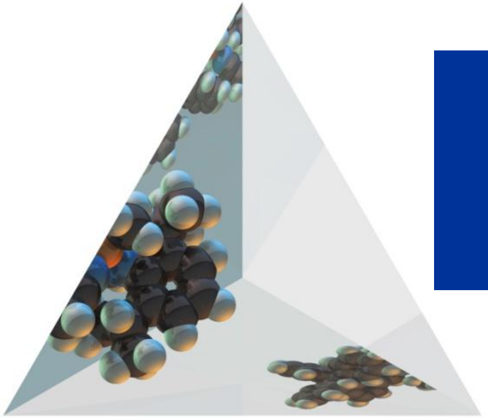
Heat Flow:

+ is **into system**

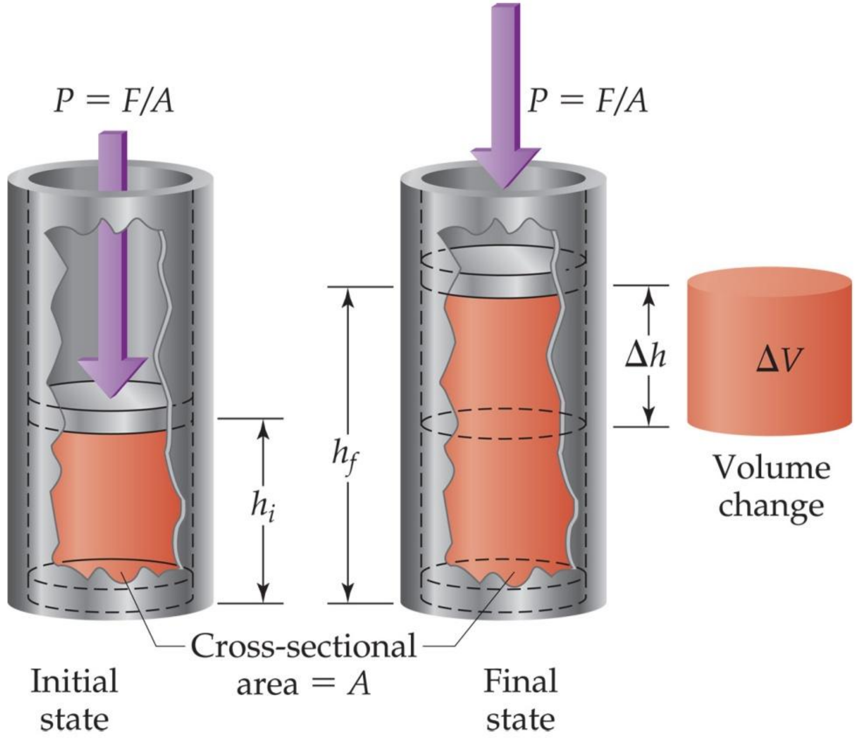
- **is** out of system

Work: + is done **on system**

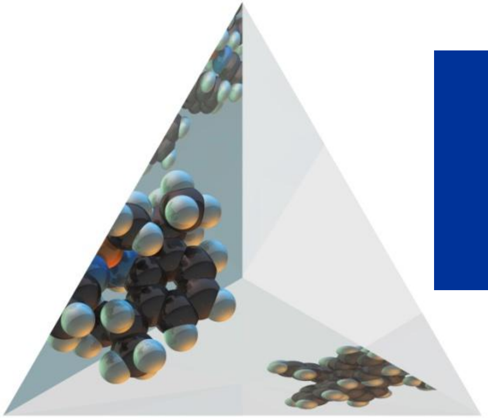
- is done **by system**



Work



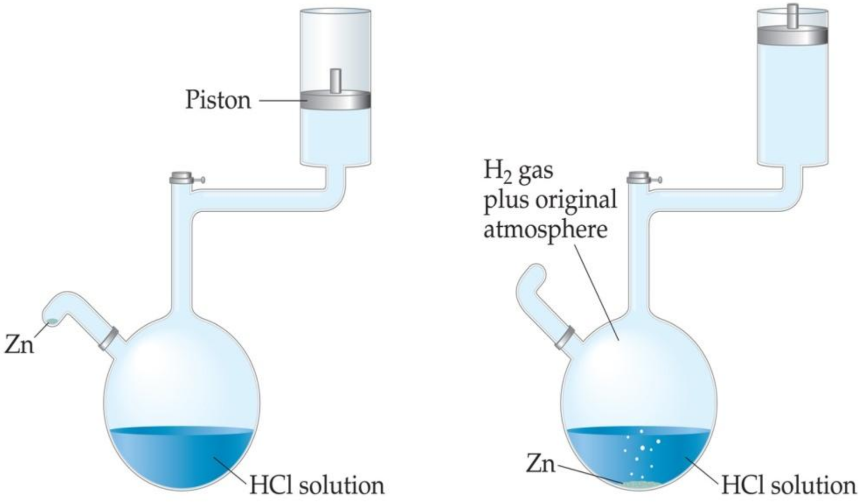
When a process occurs in an open container, commonly the only work done is a change in volume of a gas pushing on the surroundings



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.

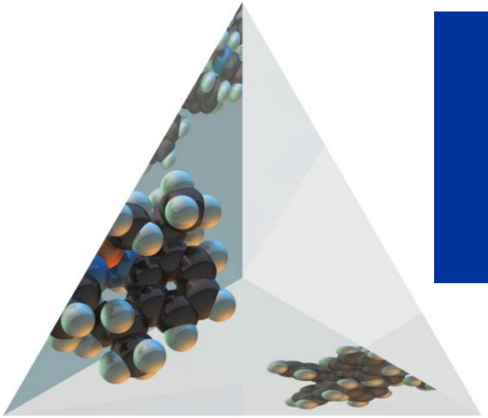
$$w = -P\Delta V$$



$$\Delta E = q + w = q - P\,\Delta V$$

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

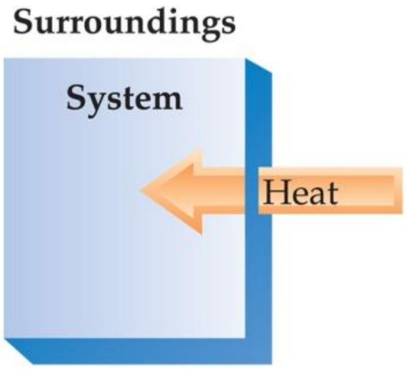
Sign Convention for q:	**Sign of $\Delta E = q + w$**
$q > 0$: Heat is transferred from the surroundings to the system	$q > 0$ and $w > 0$: $\Delta E > 0$
$q < 0$: Heat is transferred from the system to the surroundings	$q > 0$ and $w < 0$: The sign of ΔE depends on the magnitudes of q and w
Sign Convention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



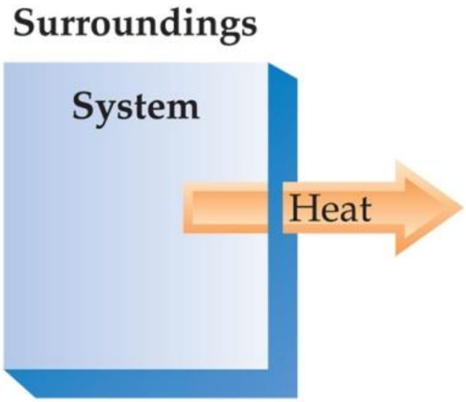
The First Law of Thermodynamics

Exothermic and Endothermic Processes

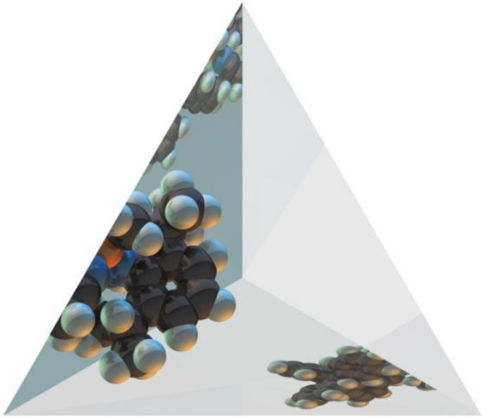
- Endothermic: absorbs heat from the surroundings.
- Exothermic: transfers heat to the surroundings.



$\Delta H > 0$
(Endothermic)



$\Delta H < 0$
(Exothermic)

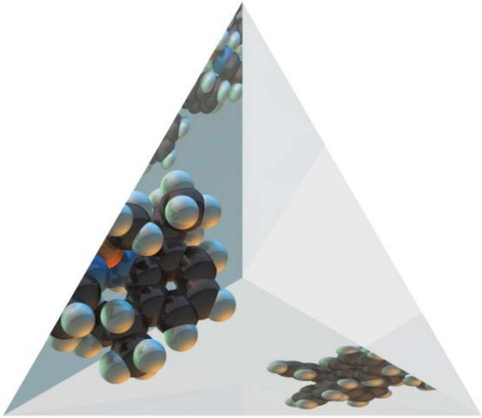


Enthalpy

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

$$H = E + PV$$

- Change in enthalpy (ΔH) is the heat gained or lost by the system when a process occurs under constant pressure.
- Only the change in enthalpy (ΔH) can be measured.



Enthalpies of Reaction

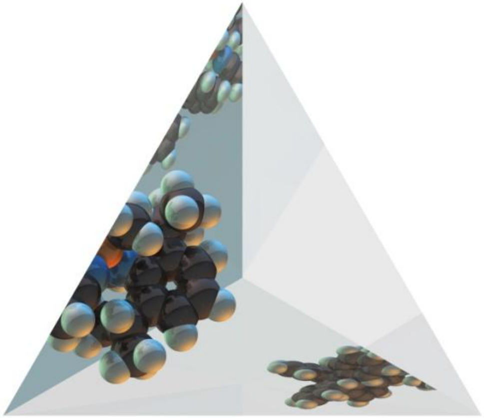
- For a reaction:

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

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

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

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



Enthalpies of Reaction

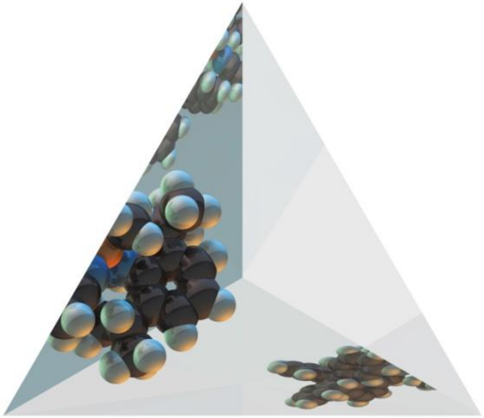
- When we reverse a reaction, we change the sign of ΔH:

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

Endothermic

- Change in enthalpy depends on state:

$$H_2O(g) \rightarrow H_2O(l) \quad \Delta H = -88 \text{ kJ}$$



Calorimetry

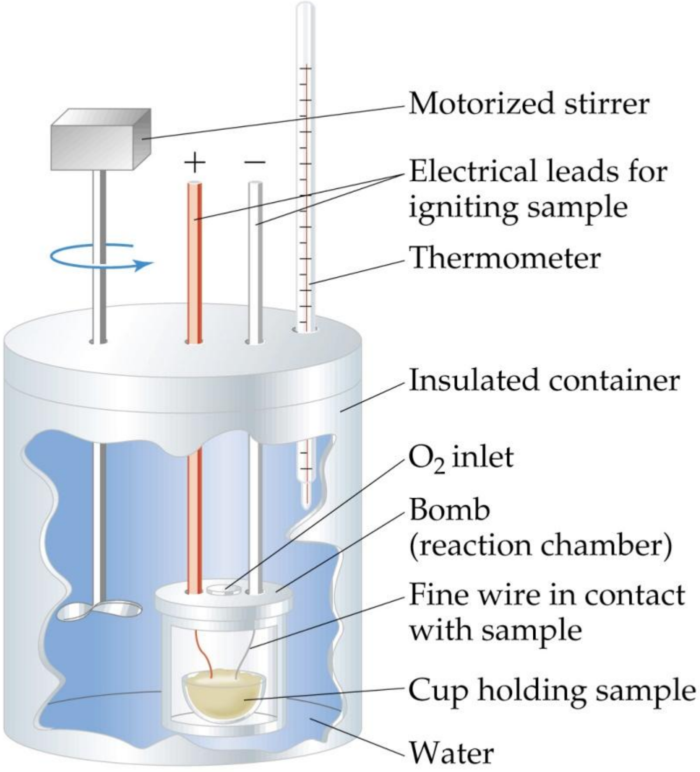
Heat Capacity and Specific Heat

- Calorimetry is a method of measuring heat flow between systems and surroundings (Calorimeter).
- Heat capacity = the amount of energy required to raise the temperature of an object (by one degree) (J/^{o}C).
- Molar heat capacity = heat capacity of 1 mol of a substance (J/mol-°C).
- Specific heat = specific heat capacity = heat capacity of 1 g of a substance (J/g-°C) .

Calorimetry

Constant Pressure and Bomb Calorimetry

- The device used to measure heat flow between systems and surroundings is called a calorimeter.

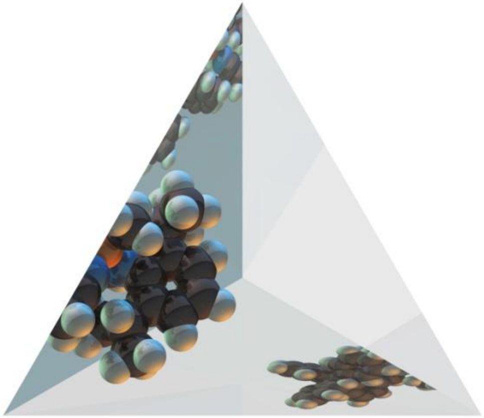


$$\text{Specific heat capacity (C)} = \frac{\text{quantity of heat supplied}}{(\text{mass of object}) \cdot (\text{temperature change})}$$

$$C = \frac{q(J)}{[m(g)] \cdot [\Delta T(K)]}$$

Specific Heats for Some Subst's at 298K

H_2O (l)	4.18 $J.K^{-1}g^{-1}$
N_2 (g)	1.04 $J.K^{-1}g^{-1}$
Al (s)	0.90 $J.K^{-1}g^{-1}$
Fe (s)	0.45 $J.K^{-1}g^{-1}$
Hg (l)	0.14 $J.K^{-1}g^{-1}$



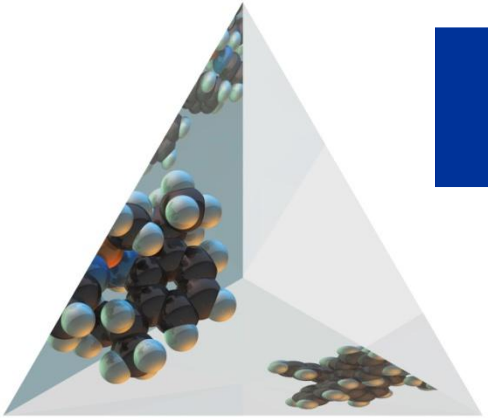
Hess's Law

- **Hess's law**: if a reaction is carried out in a number of steps, ΔH for the overall reaction is the sum of ΔH for each individual step.
- For example:

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

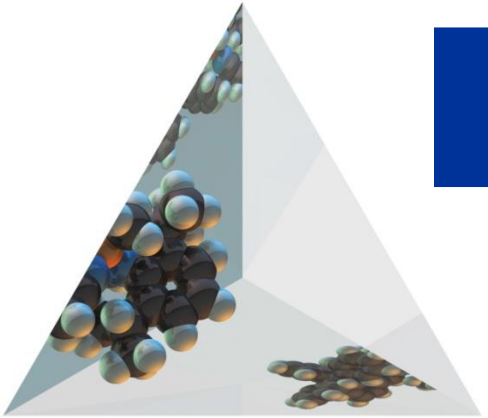
$$2H_2O(g) \rightarrow 2H_2O(l) \qquad \Delta H = -88\text{ kJ}$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \quad \Delta H = -890\text{ kJ}$$



Enthalpies of Formation

- An enthalpy of formation, ΔH^{o}_{f}, is defined as the enthalpy change for the reaction in which a compound is made from its constituent elements in their elemental forms.
- Standard enthalpies of formation are measured under standard conditions (25°C and 1.00 atm pressure)(kJ/mol).
- $\Delta H^{o}_{f} = 0$ kJ/mol for the most stable form of any element



Enthalpies of Formation

- If there is more than one state for a substance under standard conditions, the more stable one is used.

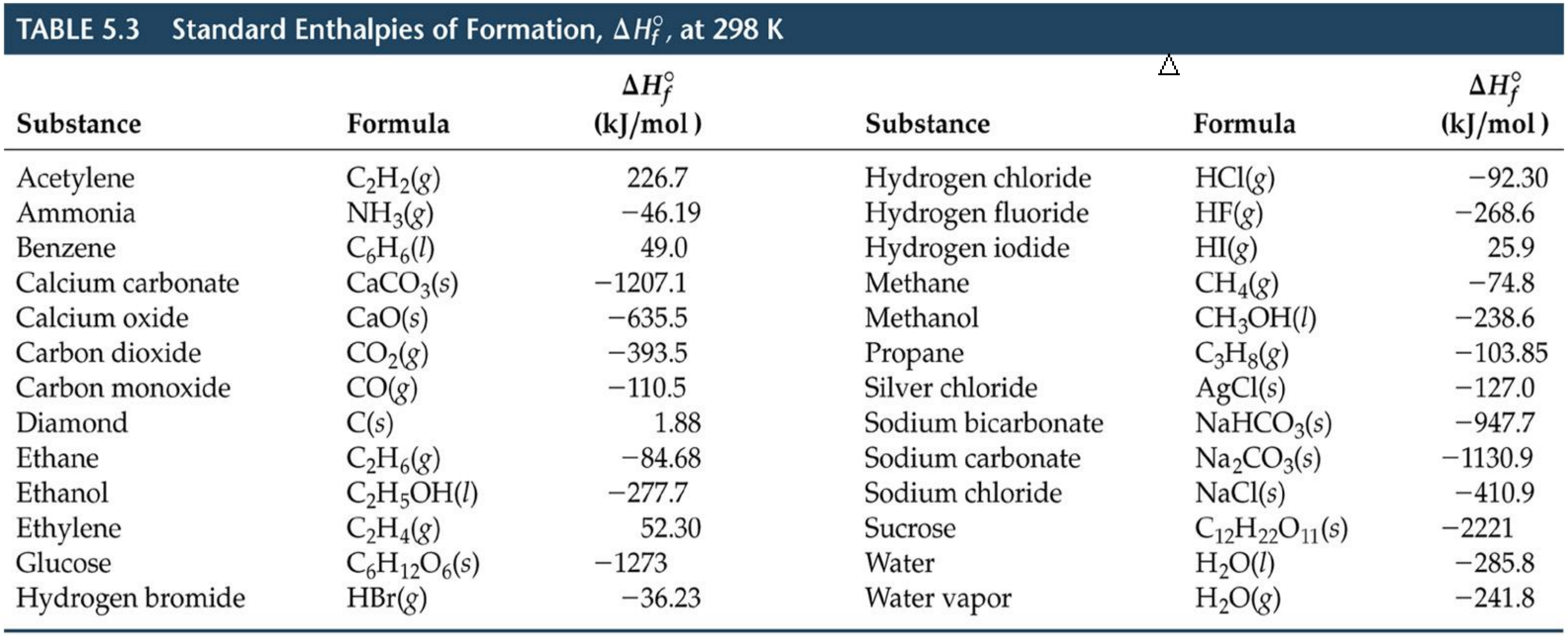
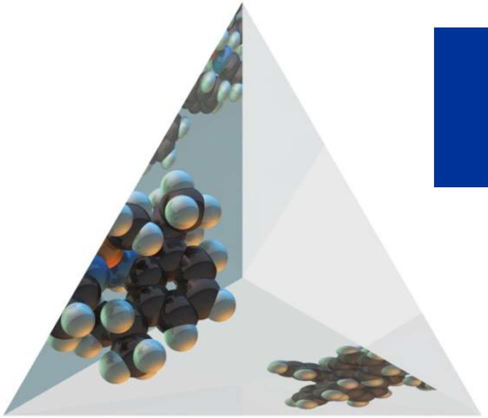


TABLE 5.3 Standard Enthalpies of Formation, ΔH_f°, at 298 K

Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	−92.30
Ammonia	$NH_3(g)$	−46.19	Hydrogen fluoride	$HF(g)$	−268.6
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	−1207.1	Methane	$CH_4(g)$	−74.8
Calcium oxide	$CaO(s)$	−635.5	Methanol	$CH_3OH(l)$	−238.6
Carbon dioxide	$CO_2(g)$	−393.5	Propane	$C_3H_8(g)$	−103.85
Carbon monoxide	$CO(g)$	−110.5	Silver chloride	$AgCl(s)$	−127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	−947.7
Ethane	$C_2H_6(g)$	−84.68	Sodium carbonate	$Na_2CO_3(s)$	−1130.9
Ethanol	$C_2H_5OH(l)$	−277.7	Sodium chloride	$NaCl(s)$	−410.9
Ethylene	$C_2H_4(g)$	52.30	Sucrose	$C_{12}H_{22}O_{11}(s)$	−2221
Glucose	$C_6H_{12}O_6(s)$	−1273	Water	$H_2O(l)$	−285.8
Hydrogen bromide	$HBr(g)$	−36.23	Water vapor	$H_2O(g)$	−241.8

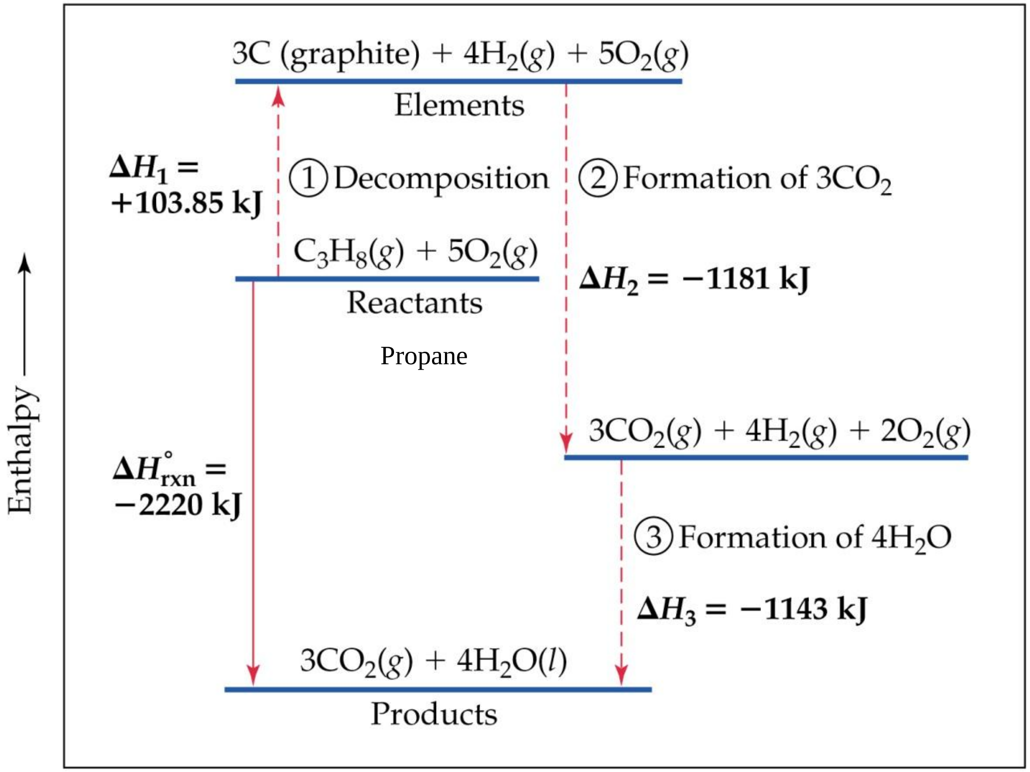
Appendix C in your textbook contains ΔH°_f

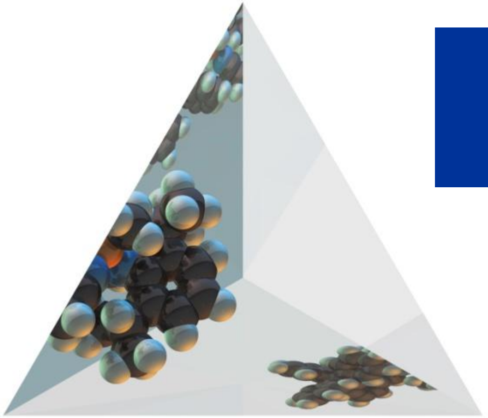


Enthalpies of Formation

Using Enthalpies of Formation of Calculate Enthalpies of Reaction

- We use Hess’ Law to calculate enthalpies of a reaction from enthalpies of formation.





Enthalpies of Formation

Using Enthalpies of Formation of Calculate Enthalpies of Reaction

- For a reaction

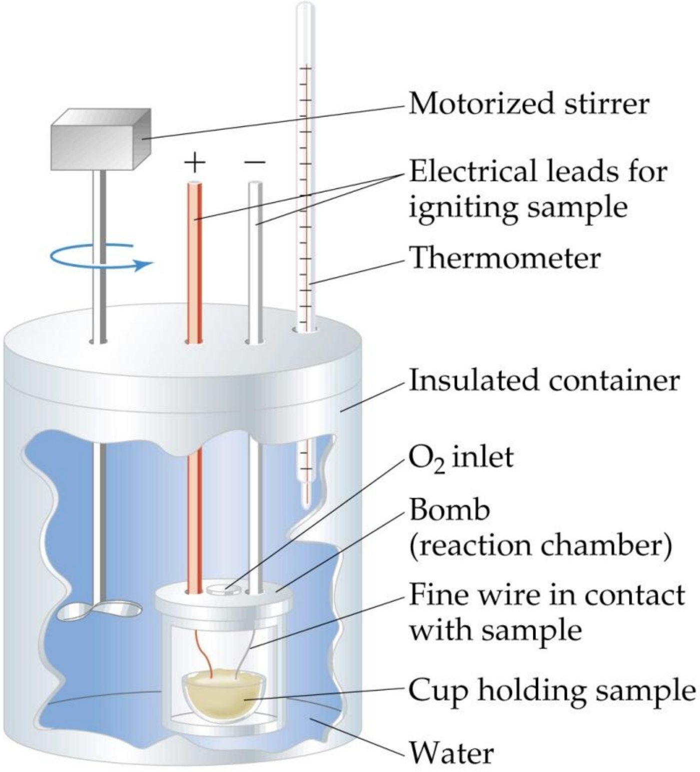
$$\Delta H^\circ_{\text{rxn}} = \sum n\Delta H^\circ_f(\text{products}) - \sum m\Delta H^\circ_f(\text{reactants})$$

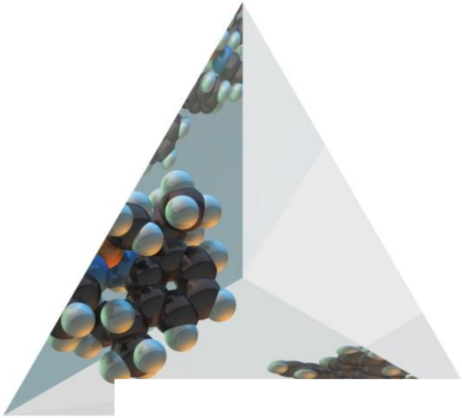
where *n* and *m* represent the coefficients in a balanced chemical equation,

Calorimetry

Constant Pressure and Bomb Calorimetry

- The device used to measure heat flow between systems and surroundings is called a calorimeter.





$$q_{\text{system}} = q_{\text{water}} + q_{\text{bomb}} + q_{\text{rxn}} \\ = 0 \tag{6.5}$$

where q_{water}, q_{bomb}, and q_{rxn} are the heat changes for the water, the bomb, and the reaction, respectively. Thus

$$q_{\text{rxn}} = -(q_{\text{water}} + q_{\text{bomb}}) \tag{6.6}$$

The quantity q_{water} is obtained by

$$q = ms\Delta t$$

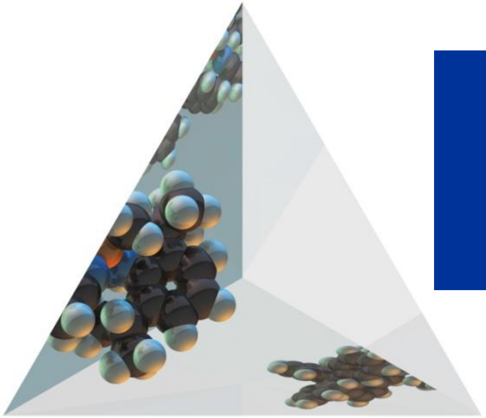
$$q_{\text{water}} = (m_{\text{water}})(4.184\ \text{J/g}\cdot{}^{\circ}\text{C})\Delta t$$

The product of the mass of the bomb and its specific heat is the heat capacity of the bomb, which remains constant for all experiments carried out in the bomb calorimeter:

$$C_{\text{bomb}} = m_{\text{bomb}} \times s_{\text{bomb}}$$

Hence

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



How to obtain C_{cal}

- Benzoic acid ($C_7H_6O_2$)
- 1.000g benzoic acid=26.38kJ of heat