Thermodynamic Definitions

- Thermodynamics is the science of heat and work. It is a precise quantitative subject whose concepts must be defined carefully. One fundamental motion is the **state of a system**. In thermodynamic analyses, we often describe the state of a system or changes in the state of a system, but what do we mean by system and state?

Thermodynamic Definitions

- A thermodynamic **system** is any part of the universe that we want to describe and study by itself. For example, an automobile, a thundercloud or the earth. After we have selected a particular thing to be a system, the rest of the universe is defined to be the **surroundings**.

  System + Surroundings = Universe

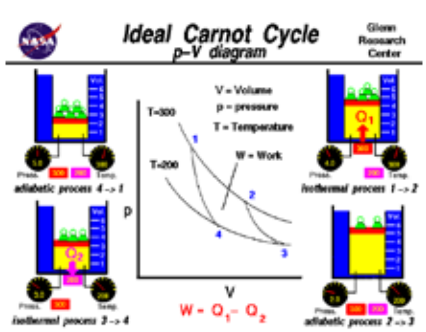
Thermodynamic Definitions

- The conditions that describe a system are collectively called its state. When these conditions change, we speak of a **change of state**. Conditions that must be specified to establish the state of a system are called **state variables**. For chemical systems, variables are often familiar quantities:

Pressure (P), Volume (V), Temperature (T), amounts of substances (n).

Thermodynamic Definitions

- Frequently, state variables are related in some way. A mathematical equation that describes such a relationship is an equation of state (e.g. PV = nRT). Changes of state occur during most interesting processes in thermodynamics.



Energy

- Energy is the foundation of thermodynamics. It is neither created nor destroyed in any process although it may be transferred from one body to another or converted from one form into another.
- **Energy is ALWAYS conserved.**
- **Energy is the capacity to do work or move matter.**
- **Energy-releasing reactions are said to be exothermic.**
- **Energy-absorbing reactions are said to be endothermic.**

Energy

- The understanding of energy flow and conservation is complicated because energy takes on several different forms. Kinetic, potential, thermal and radiant energy all play important roles in chemistry.

Kinetic and Potential Energy

- Any moving object possesses energy of motion which is called kinetic energy (KE). KE varies with the mass of the body and the velocity at which it is moving.

$KE = mv^2/2$

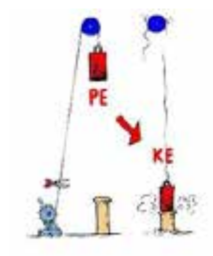
The eq. states that the units for E be (mass)(distance)^2 (time)$^{-2}$, so the SI unit for KE is (kg)(m)^2(s)$^{-2}$. It always has these same dimensions and units. It is called the Joule (J).

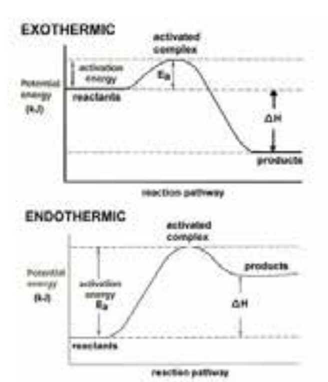
Energy = (mass)(distance)^2/(time)^2 = (kg)(m)^2/(s)^2 = Joules (J).

Kinetic and Potential Energy

- **Potential energy (PE)** is stored energy. For example, a rock teetering high on a ledge is about to release stored gravitational energy, a cloud on the verge of "hurling" a thunderbolt earthward is about to release stored electrical energy and gasoline in the cylinder of your car engine is about to release stored **chemical energy**. In each case, the stored energy is called PE.

Kinetic and Potential Energy





Energy and Heat

- In chemistry, one of the most important forms of E is thermal motion. A change in thermal motion of a system requires a flow of E and a transfer of thermal energy is known as **heat (q)**. Heat transfers are changes in E so they are measured in Joules (J).
- A flow of heat frequently causes a temperature (T) change. T is not E but it is related to E. A change in an object's T (ΔT) depends on three factors:

Energy and Heat

- 1. ΔT depends on q, the amount of heat that has been transferred. That is, the transfer of 50 J of heat to an object causes an increase in T that is twice as large as the increase caused by 25 J of heat.
- 2. ΔT depends on the amount of material. That is, the transfer of 50 J of heat to 1 mol of a substance causes a T increase that is twice as large as the increase caused by the transfer of 50 J of heat to 2 mol of the same substance.
- 3. ΔT depends on the identify of the material. For instance, 50 J of heat increases the T of 1 mol of Au more than it increases the T of 1 mol of water.

Energy and Heat

- This sensitivity to heat is expressed by a quantity called the:
- **specific heat capacity (C)** – the ratio of the heat supplied to some mass of the substance (say, 1.00 g) to the consequent rise in the substance's T.

$$C = q / m\Delta T$$

- **molar heat capacity (C_p)** – the heat needed to reaise the T of 1 mol of substance by one kelvin (1 K).

$$C_p = q / n\Delta T$$

Energy and Heat

- In both these equations, q is the heat transferred, m is the mass of material involved and n is the number of moles of material involved.
- These eqns. tell us that the larger C and, hence, C_p are, the more thermal E the substance can store. Also, substances with a high C and C_p cool down more slowly than those with a smaller C and C_p.

Problems

- An aluminum frying pan that weighs 745 g is heated on a stove from 25^{o}C to 205^{o}C. What is q for the frying pan?
- A thirsty marathon runner pours 200 mL of Gatorade from a can at 25^{o}C. What is the minimum mass of ice that must be added to cool the drink to 0^{o}C?

Problems

- Phoebe's insulated foam cup is filled with 150ml of coffee at (c = 0.907 cal/*g* °*C*) 70 °C. It is too hot to drink, so she adds 10ml of milk (c = 0.907 cal/*g* °*C*) at 5.0°C. What is the final temperature of the coffee and milk mixture? (hint: treat it like a water mixing problem)
- Emily is testing her baby's bath water and finds that it is too cold so she adds some hot water from a kettle on the stove. If Emily adds 2.00kg of hot water at 80°C to 20kg of bath water at 27°C, what is the final temperature of the bath water?

First Law of Thermodynamics

- E can be transferred as heat or work. Heat and work can be transferred into or out of a system. During a chemical rxn, changes in chemical E may cause heat transfer and/or work transfer. Because E must be conserved, the E change of the system is linked to the flow of heat and work:

$$\Delta E_{sys} = q_{sys} + w_{sys}$$

First Law of Thermodynamics

- Scientists have found that heat and work transfers are sufficient to account for the E change that accompanies any process.

$\Delta E_{sys} = q_{surr} + w_{surr} = (-q_{sys}) + (-w_{sys})$

$= -(q_{sys} + w_{sys}) = \Delta E_{sys}$

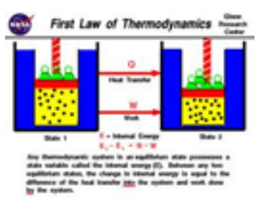
This expression is a restatement of the law of conservation of E: Any change in the E of a system must be counterbalanced by an opposite change in the E of the surroundings.

First Law of Thermodynamics

- The 1st law of thermodynamics states that ΔE, the E change of any *system*, is equal to the heat absorbed by the system plus the work done on the system. Any heat absorbed by the system increases the system's E and any work done on the system likewise increases the system's E. The *surroundings* must provide this E if the total E of the universe is to be conserved. Thus, as the system absorbs heat, the surroundings lose E, and as work is done on the system, the surroundings lose the E needed to do that work. A system often

First Law of Thermodynamics

- undergoes a change in E during a process but the surroundings undergo an equal and opposite change in E so the total E of the universe remains unchanged.



Calorimeter

- A device that measures heat flow is called a calorimeter. In a calorimetry experiment, a set of chemicals undergoing a change in E is enclosed in the water bath. The calorimeter and the chemical that it contains act as an isolated system because the insulation blocks the flow of heat between system and surroundings:

Calorimeter

- $q_{surr} = q_{sys} = 0$

So,

- $q_{sys} = q_{calorimeter} + q_{chemicals} = 0$

Thus,

- $q_{chemicals} = -q_{calorimeter}$

and

$q_{calorimeter} = C_{cal}\Delta T$

Total heat capacity of the calorimeter is usually determined by measuring ΔT that accompanies the transfer of a known amount of heat.

Calorimeter

Problems

- A calorimeter is calibrated using an electrical heater. Before turning on the heat, the calorimeter is 23.55ºC. The addition of 10.00 kJ of electrical E raises the T to 24.67ºC. Determine the total heat capacity of this calorimeter.
- Ammonium nitrate (NH_4NO_3) is a salt used in cold packs for icing injuries. When 20.0 g of this salt dissolves in 125 g of water in a coffee-cup calorimeter, the T falls from 23.5ºC to 13.4ºC. Is the chemical process exothermic or endothermic? Determine q for the calorimeter.

Problem

- When a 1.000 g sample of the rocket fuel hydrazine, N_2H_4, is burned in a bomb calorimeter which contains 1200 g of water, the temperature rises from 24.62°C to 28.16°C. If the C for the bomb is 840 J/°C, calculate
- $q_{reaction}$ for combustion of a one-gram sample
- $q_{reaction}$ for combustion of one mole of hydrazine in the bomb calorimeter

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^+