The First Law of Thermodynamics

- The ***First Law of Thermodynamics*** states that the ***energy of an isolated system is constant.***

- If a system does an amount of work *w,* its internal energy (*U*) falls by the amount *w*. Similarly, if an amount *q* of heat leaks away from the system, its internal energy falls by an amount *q.* These are the only ways of changing the internal energy of a closed system.

- Let the work done on a system be the infinitesimal amount d*w,* and the heat added be the infinitesimal amount d*q*. Then the infinitesimal increase in the internal energy of the system d*U* is related by: $dU = dq + dw$ (First Law).

- The above is the mathematical expression of the First Law. It expresses the observation that the internal energy of a closed system changes by the amount of work and the heat transferred through its walls, and that these changes account for any change of the internal energy.

- The simplest processes are those in which *P*, *V*, or *T* change. A constant temperature process is referred to as ***isothermal***; constant *P* is called ***isobaric***; constant *V* is called ***isochoric***.

The Sign Convention

- We use the convention that d*q* denotes the *heat added to* the system, and d*w* denotes the *work done on* the system
  - both d*q* and d*w* denote contributions to the internal energy of the system.
- *When* d*q* *has a positive value* it signifies that heat has been transferred to the system and that it has contributed to an increase in the internal energy.
  - *when* d*q* *has a negative value*, it signifies that heat has flowed out of the system and that this has contributed to a decrease in the internal energy
  - if the system gains an amount of heat d*q*, the surroundings lose that amount (or gain -d*q*).
- *When* d*w* *has a positive value* it signifies that work has been done on the system and that it has contributed to an increase in the internal energy
  - *when* d*w* *has a negative value*, it signifies that work has been done by the system on the outside world, and that this has contributed to a decrease in the internal energy
  - if the system does an amount of work on the outside world, it is incorporated into the scheme by saying that the negative of that amount was done on the system.

Work

Mechanical Work

• When an object is displaced through a distance d*x* against a force *F*(*x*) the amount of work that has to be done on it is **d*w* = - *F*(*x*) d*x***

- if the force pushes towards +x (opposing motion to the left) it is positive; if it pushes towards –x (opposing motion to the right) it is negative

- if the force is constant: $$w = -\int_{x_i}^{x_f} F\,\mathrm{d}x = -(x_f - x_i)F$$

If the constant force opposes motion to the right, *F* is negative:

$$w = +(x_\mathrm{f} - x_\mathrm{i})|F|$$

If the final position x_f lies to the right of x_i ($x_\mathrm{f} > x_\mathrm{i}$) *w* is positive: work has to be done on the object to move it against the force.

- if the force varies from point to point, e.g. gravitational force ($-GmM/x^2$). The amount of work required to raise a mass *m* from the surface of the earth (mass *M*) to an altitude where the gravitational attraction is negligible (*G* is the gravitational constant, *R* is the radius of the earth):

$$w = -\int_R^\infty (-GmM/x^2)\,\mathrm{d}x = GmM\int_R^\infty (1/x^2)\,dx = GmM/R$$

(calculation neglects air resistance).

Heat

- Heat is defined in thermodynamics as the quantity of energy that flows across the boundary between the system and surroundings because of a temperature differential.

- Just as case work, heat is transitory in that it only appears during a change in state of the system and surroundings. *Only energy, and not heat, is associated with the initial and final states of the system and the surrounding.*

- The internal energy of a system rises when heat is transferred into it. If an amount d*q* of heat is allowed to pass through the walls, the rise in internal energy is **d*U* = d*q***

- When heat is added to a system its temperature rises. For an infinitesimal transfer of heat the rise in temperature is proportional to the amount of heat supplied: **d*T* ∝ d*q*, or d*T* = constant x d*q***, the value of the constant depending on the composition and temperature of the system.

- The above equation, with the constant, is more conveniently represented inverted: **d*q* = *C* d*T*.** The constant ***C*** is called the ***heat capacity*** of the system.

Heat Capacity

• When the heat capacity, ***C***, ***is large*** the transfer of a given amount of heat to a system leads to only ***a small rise in temperature***; but when it is ***small*** the same amount of heat can cause a ***large rise in temperature.***

• The magnitude of *C* depends on the size of the system: a bigger body requires more heat than a small body to bring about the same rise of temperature (*C* is in the SI units of JK^{-1}). The heat capacity of 1 mol of material is written C_m and called the ***molar heat capacity.***

• The heat capacity also depends on the conditions under which the heat is transferred into the system

- if the system is constrained to a constant volume: the heat required to bring about a rise in temperature d*T* is some amount $C_v dT$
- if the system is permitted to expand (or contract) as the heat is added, the amount required to bring about the same rise in temperature is $C_p dT$ (constant pressure) (in this case the system ***has also done some work*** because of the change in size).

$$C_V = \frac{dq}{dT} \text{ at constant volume} = \left(\frac{\partial q}{\partial T}\right)_V$$

$$C_P = \frac{dq}{dT} \text{ at constant pressure} = \left(\frac{\partial q}{\partial T}\right)_P$$

Heat Capacity

Example Problem (not in textbook)

Find the partial derivative of P with respect V and T for van der Walls equation of state (for a unit mole):

$$P(V,T) = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}; \quad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

Note that $$\frac{\partial^2 P}{\partial V \partial T} = \frac{\partial^2 P}{\partial T \partial V}$$

What is Work, and What is Heat?

• We identify thermodynamic internal energy with molecular energy. Molecular energy resides in the strength of molecular bonds and in the molecular translation, vibration and rotation.

• Heat is a way of increasing internal energy because it stimulates molecular motion. When an object is heated the molecular motion occurs in random directions. Heat stimulates random motion. We call this random motion thermal energy.

• Work involves organized motion. When a spring is compressed the atoms move close together in a definite direction, and they move apart in a definite direction when it unwinds. Work stimulates organized motion.

• When a gas is compressed isothermally (so that the initial temperature is maintained by the heat flow) the accelerated molecules strike the conducting walls of the vessel, and its atoms are excited into vibration. This jostling is handed on to the outside world. The work of compression has been degraded into the thermal energy of the surroundings.

• When a gas is compressed adiabatically (so that no heat enters or leaves the system) the accelerated molecules strike insulating walls, which are unable to transmit thermal energy out of the system. The rise in internal energy appears as a rise in the temperature of the compressed gas, and is stored as the thermal energy of the system.