

2.1 CONSERVATION OF ENERGY

In mechanics we defined energy of a particle of mass m as the sum of kinetic energy and potential energy.

$$E = K.E. + P.E. = \frac{1}{2}mv^2 + U. \quad (2.1)$$

The energy of a multi-particle system is obtained by summing the energies of each particle. The potential energy due to internal forces between the particles of the system need to be included only once for each pair.

$$E = K.E. + P.E. = \sum_i \frac{1}{2}m_i v_i^2 + \sum_{\langle i,j \rangle \text{ pair}} U_{int}(\vec{r}_i, \vec{r}_j) + \sum_i U_{ext}(\vec{r}_i), \quad (2.2)$$

where U_{int} is potential energy of the system due to internal forces between particles of the system and U_{ext} is the potential energy due to external forces, such as gravity, on the particles. We have shown the energy of an isolated system does not change with time. That is, the change in energy ΔE of an isolated system over a duration Δt

$$\Delta E = 0 \quad \text{for an isolated system.} \quad (2.3)$$

If a system is not isolated, the system will exchange energy with other systems it interacts with. Suppose two isolated systems A and B interact with each other. But since the two systems together are isolated, their combined energy will not change with time. Any gain in energy of system A will be equal in magnitude to the loss of energy of the system B.

$$\Delta E_A = -\Delta E_B, \quad (2.4)$$

where

$$\Delta E_A = \Delta(K.E.)_A + \Delta(P.E.)_A, \quad (2.5)$$

and similarly for ΔE_B . In principle, we can obtain the energies of systems A and B from the kinetic and potential energies of the constituent particles in the form given in Eq. 2.2. The trouble comes from the fact that ordinary objects contain a very large number of particles. For instance, 63.5 g of copper contains 6.022×10^{23} atoms. Clearly, it is not possible to keep track of kinetic energy of each atom and the interaction energies between the atoms. Fortunately, we do not need to know the exact energy of any system, but only the change in energy. Thermodynamics provides another way to account for energy change.

We have seen that in thermodynamics, two systems in thermal contact can exchange energy when they are not in a thermodynamic

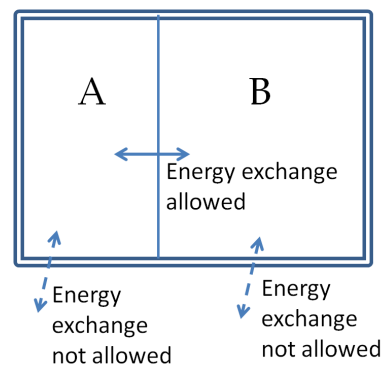


Figure 2.1: Systems A and B are closed systems that exchange energy but the two systems together form an isolated system.

equilibrium. For instance, if the two systems in thermal contact are at different temperatures they will exchange energy, called heat, until the two systems reach the same temperature. Similarly, if two systems are not in mechanical equilibrium, they will do work on each other until the two come to the mechanical equilibrium, and if two systems, which can freely exchange chemicals, will exchange energy until the chemical potentials of each chemical entity is same in the two systems.

Therefore, in place of the change in the kinetic and potential energies of the particles of a system, we can account for the energy exchanged between two systems in terms of heat, work and energy associated with chemical potential.

Consider again the two closed systems A and B that interact with each other but the combined system is isolated. The change in energy of system A can be written in terms of heat and work as follows,

$$\Delta E_A = Q_{B \rightarrow A} - W_{A \rightarrow B}, \quad (2.6)$$

where heat into A is positive and work by A is positive, and I have assumed that the chemical composition of A does not change. The energy of the other system, system B, will change accordingly.

$$\Delta E_B = Q_{A \rightarrow B} - W_{B \rightarrow A}, \quad (2.7)$$

Equations 2.6 and 2.7 are the statements of the **first law of thermodynamics** of the closed systems A and B respectively. You might say that they are nothing more than the conservation of energy expanded to include the possibility of energy exchange when two systems are in thermal contact also. And you would be right.

2.1.1 First Law of Thermodynamics and Internal Energy

Often in thermodynamics, we remove the energies associated with the motion of the whole body from both sides of Eqs. 2.6 and 2.7. The energies removed are the kinetic and potential energies of the center of mass(CM), E_{cm} , and the energy of rotation of the entire body about CM, $E_{\text{cm}}^{\text{rot}}$. The remaining energy is called the **internal energy**. The internal energy is usually denoted by the symbol U, which should not be confused with the same symbol used for the potential energy. Thus, the internal energy of system A will be

$$U_A = E_A - [E_{\text{cm}} + E_{\text{cm}}^{\text{rot}}] \quad (2.8)$$

To obtain an equation for the internal energy, we must take away the work done on the system that changes the kinetic and potential energies of the CM and the rotation of the entire body about the CM from the right side of Eqs. 2.6. We will denote this reduced work by $W_{by A}$. In terms of internal energy and reduced work we write the first law of thermodynamics for the change in the energy of the system A as

$$U_A = Q_{\text{into A}} - W_{\text{by A}}, \quad (2.9)$$

where we have denoted $Q_{A \rightarrow B}$ by $Q_{\text{into A}}$ to keep the notation for the work and heat similar. We often drop the subscripts in this equation and write it more simply as

$$\boxed{U = Q - W.} \quad (2.10)$$

This equation is often taken as the statement of the first law of thermodynamics. In order to apply this equation properly, you would need to remember the sign notation of the heat and work.

Sign conventions:

- Heat entering into the system: $Q > 0$.
- Heat leaving the system: $Q < 0$.
- The system expanding: $W > 0$.
- The system contracting: $W < 0$.

Further Remarks: Yet another approach to energy conservation is based on the various types of energy sources in common vernacular use. For instance, some chemical reactions release energy, we call that energy to be Chemical Energy. Similarly, the energy in a nuclear reaction is called the Nuclear Energy. Classifying energy into various types is helpful in this regard since an overall energy of each type can often be determined from experiments. The change in internal energy is then written as a sum of

$$\Delta U = \Delta E_{\text{chem}} + \Delta E_{\text{nuc}} + \Delta E_{\text{atom}} + \cdots \quad (2.11)$$

where various terms have the following interpretation.

- Chemical energy, E_{chem} ,
- Nuclear energy, E_{nuc} ,
- Atomic random motion, E_{atom} , etc

2.1.2 Adiabatic Work and Internal Energy

Joule conducted experiments on the effect of stirring on the change in the state of water as determined from the change in the temperature

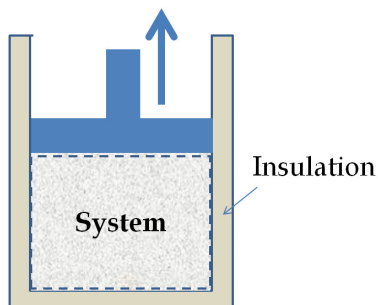


Figure 2.2: Adiabatic expansion. In an adiabatic expansion, there are two time scales: the rate of the process and the rate at which heat may enter the system through the walls, i.e. boundaries of the system. If the expansion occurs within a time frame in which only negligible heat can enter or exit the system, then the process is called **adiabatic**. Ideally, during an adiabatic process no heat will enter or exit the system.

of water. He found that if the container is insulated so that heat cannot flow in or out of the stirred water, the amount of work associated with the change of the state of water from an initial state i to a final state f was independent of how the work was performed. That is, the work done by the system under adiabatic conditions does not depend on the path; it depends only on the initial and final states.

When a system expands adiabatically, it must do work against the outside world, and therefore its energy goes down, which is reflected in the lowering of the temperature of the system. Thus, we say that the change in the internal energy is equal to the work done on the system when the system goes from an initial state i to a final state f under adiabatically conditions.

$$\boxed{W_{if}^{\text{on system}} = U_f - U_i \quad (\text{Adiabatic})} \quad (2.12)$$

Microscopically, a positive work done on a system which is thermally insulated goes towards increasing the kinetic and potential energies of molecules in random motion, thereby increasing the internal energy of the system. A negative work on the system will be the same as a positive work by the system. A negative work on an insulated system will lower the kinetic and potential energies of molecules thereby lowering the internal energy.