

Physical Chemistry

Lecture 7

Internal energy, work and heat

Energy

- ◆ Useful in determining a wide variety of processes
- ◆ Total energy (U) is an extensive variable

$$U = K.E. + P.E.$$

- ◆ Can define the intensive variable, U_m
- ◆ Two ways to change the internal energy

$$\Delta U = q + w$$

- Mechanical – work (w)
- Heat transfer – heat (q)

First law of thermodynamics

- ◆ The internal energy, U, of a system remains constant unless work is done on (by) it or heat flows into (from) it.
- ◆ Conservation of energy in a process
- ◆ Internal energy is a state function independent of the path

$$U(T_2, V_{m2}) - U(T_1, V_{m1}) = \int dU_{\text{along path}}$$

Work

- ◆ Mechanical work
 - Application of a force changes the system
- $$w = \int_{\text{along path}} \mathbf{F} \cdot d\mathbf{r}$$
- ◆ Other kinds of work
 - Electrical – movement of charge
 - Magnetic – creation of magnetization
 - Surface – creation of a surface
 - ◆ Work is path-dependent, i.e. how the force is applied
 - ◆ Not a state function

Work

- ◆ Total work
 - Sum of all contributions in a process
- $$w = w_{\text{mech}} + w_{\text{elect}} + w_{\text{magn}} + w_{\text{surface}} + \dots$$
- ◆ Often consider problems in which only a single kind of work is important to simplify it
 - Bulk-gas problems – mechanical work
 - Electrochemical systems – electrical work
 - Surface systems – creation of surface

Mechanical work

- ◆ May change volume by moving a wall
 - ◆ Requires force
- $$dw_{\text{mech}} = - F d\ell$$
- Work is positive when done ON the system
 - Hence, the negative sign

$$dw_{\text{mech}} = - F \frac{A}{A} d\ell = - \frac{F}{A} (A d\ell) = - PdV$$

Heat flow

- ◆ Energy, q , added by means other than work
 - Radiation through the walls
 - Heat conduction through walls
- ◆ Depends on how the heat is added, i.e. path
- ◆ Not a state function

Energy changes

- ◆ Heat flow and work are not state functions
- ◆ Total energy change is a state function
- ◆ Peculiar situation in which the sum of two path-dependent quantities is path-independent

$$\Delta U = w + q$$

Summary

- ◆ First Law is a statement of conservation of energy
- ◆ Total energy is a state function
- ◆ Changes in energy caused by heat flow or by work
- ◆ Heat flow and work are not differential state functions