Thermodynamics

TOPICS COVERED

- Modes of Heat
  - Work
  - Generalize form of workdone
  - Expansion
  - Compression
  - Work done for different processes

Modes of Energy Transfer

Energy can be transferred by two modes

(a) Work

(b) Heat

Work

- The transfer of energy between a chemical reaction system and its surroundings occurs called work or heat.
- **Work, w,** is the mechanical transfer of energy from one thing to another

$$\text{Work} = \text{Force} \times \text{Displacement}$$

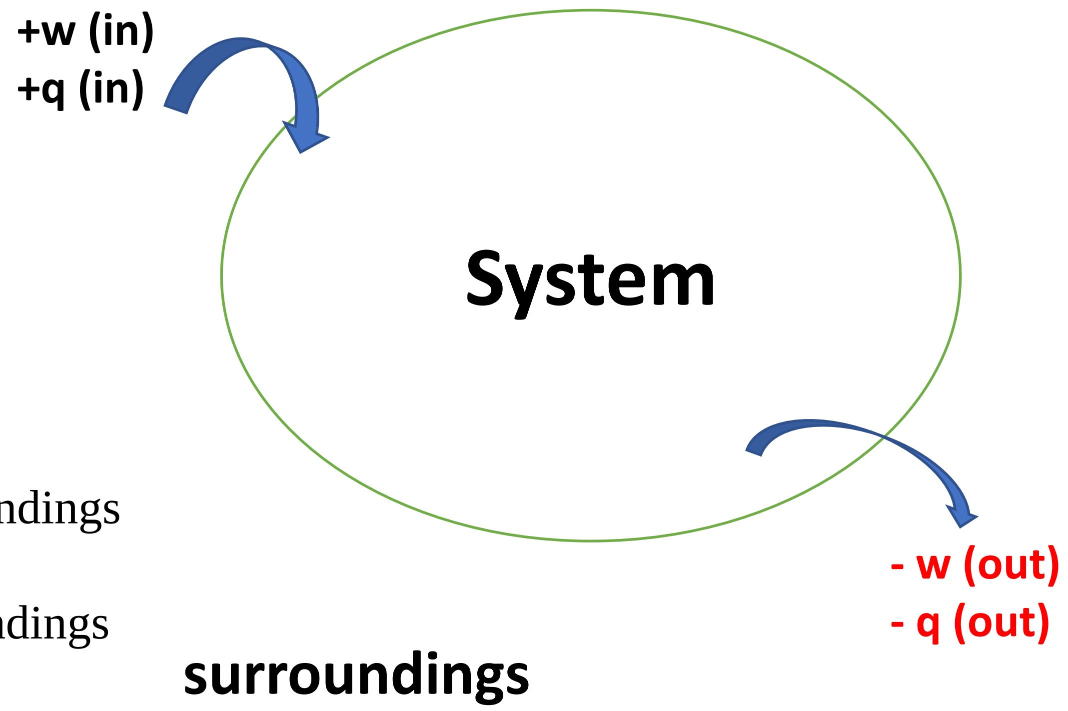
Work

- Energy transfer due to change in the volume of system on application of external pressure
- Pressure is a force over a unit area

$$P = \frac{\text{Force}}{\text{Area}}$$

(Sign Conversion)

- **+w** for work done **on** the system by the surroundings
- **-w** for work done by the system **on** the surroundings

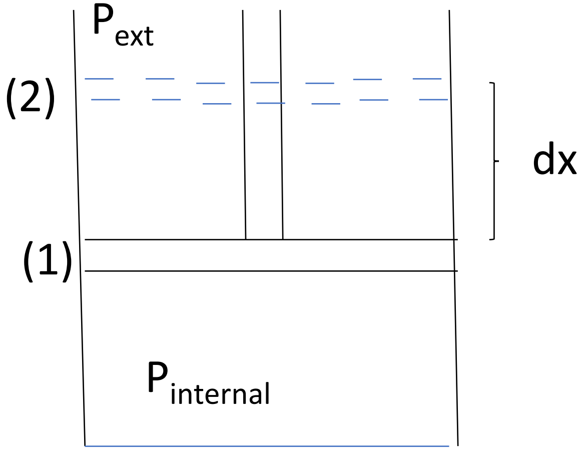


GENERALIZE FORM OF WORKDONE

- If system is a cylinder which is filed by gas having a piston then two types of work done takes place.

- Work done
  - **Expansion**- $P_{external} > P_{gas}$ - workdone is **negative**
  - **Compression**- $P_{external} < P_{gas}$ - workdone is **positive**

WORK $(w = -\int PdV)$



If $\mathbf{P_{external}} < \mathbf{P_{internal}}$ (expansion) takes place then the position of piston changes from (1) to (2) so, change in position is said to be as dx

For dx displacement (change in position)

Change in volume, $dV = A \times dx$

Force against which work is done $F_{ex} = P_{ex} \times A$

So, work done $\delta w = - F_{ex} \times dx$

Put the value of F_{ex} form the above expression

$$\delta w = - P_{ex} \times A \times dx \qquad = (A \times dx = dV)$$

Change in work done

$$\delta w = - P_{ex} \times dV$$

Total work done (W)

$$W = - \int P_{external} \times dV$$

if we remove integration sign , dV changes into ΔV

$\mathbf{w = - P_{ext} \Delta V}$ where, $\Delta V = V_f - V_i$

WORK

Calculate work done for Expansion: - In expansion final volume is greater than initial volume , so $V_f > V_i$ i.e. volume is positive so, $w = - \int PdV$ (work is negative)

Calculate work done for Compress**: -** In Compress final volume is lesser than initial volume, so $V_f < V_i$ i.e. volume is negative so, $w = \int PdV$ (work is positive)

Work done for different processes

- **Work done for irreversible process i.e. the external pressure remains constant**
  - $W_{irr} = - P_{ex} (V_2 - V_1)$ (Expansion)
  - $W_{rev} = - \int P_{gas}\, dV$ (Compress)
- **Work done for isobaric process:-** $W = P(V_2 - V_1)$
- **Work done for isochoric process:-** $W = 0$
- **Isothermal reversible expansion work of an ideal gas**

$$w = -nRT \ln \frac{P_1}{P_2} = -2.303\, nRT \log \frac{P_1}{P_2}$$

$$w = -nRT \ln \frac{V_2}{V_1} = -2.303\, nRT \log \frac{V_2}{V_1}$$

- **Unit of work is joule (J)**.
    - 1 joule = 10^7 ergs or 1 erg = 10^{-7} J
    - 1 kJ = 1000 J
    - 1L-atm of energy = 24.22 cal.
    - 1 Cal = 4.18 J

- **For work**

1. Work done by the system i.e. expension = -ve
2. Work done on the system i.e. compression = +ve

SOLVED PROBLEM

- ✓ **Calculate the pressure-volume work done when a system containing a gas expands from 1.0 litre to 2.0 litres against a constant external pressure of 10 atmospheres. Express the answer in calories and joules.**

SOLUTION:

$w = -P_{ext}(V2 - V1)$

$= -(10\text{ atm})(2\,l - 1\,l)$

$= -10\,l\,atm$

$= -(10\,l\,atm) \times 24.22$

$= -242.2$ cal

But 1 calorie = 4.184 J

$w = \mathbf{-1013.3648\,J}$

SOLVED PROBLEM

- ✓ **50 J of heat is supplied to a system. Calculate the work done if the internal energy of system increases by 80J.**

$\Delta U = +q + w$

$80 = 50 + w$

$w = 30$

References

Text Books

1. Atkins, P. W. & Paula, J. de ***Atkin's Physical Chemistry***10th Ed., Oxford University Press (2014).

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2. Engel, T. & Reid, P. ***Physical Chemistry***3rd Ed. Pearson (2013).
3. Levine, I .N. ***Physical Chemistry***6th Ed., Tata Mc Graw Hill (2010)
4. Puri Sharma Pathania Physical Chemistry Book.


THANK YOU