Heat, Work, Internal Energy, Enthalpy, and the First Law of Thermodynamics

1 The Internal Energy and the First Law of Thermodynamics

- *In thermodynamics, the total energy of a system is called its internal energy (U)*
- *The internal energy is the total kinetic and potential energy of the molecules in the system*
- *The internal energy is a state function in the sense that its value depends only on the current state of the system and is independent of how that state has been prepared*
- *The change in the internal energy,*

$$\Delta U = U_f - U_i$$

- *The internal energy is an extensive property*
- *The Unit of Internal energy is joule (J), which is defined as 1 J = 1 kg m^2 s^{-2}*

1 The Internal Energy and the First Law of Thermodynamics

- *A joule is quite a small unit of energy: for instance, each beat of the human heart consumes about 1 J.*

- *Changes in molar internal energy, ΔU_m, are typically expressed in kilojoules per mole (kJ mol^{-1}).*

- *1 electronvolt (1 eV), which is defined as the kinetic energy acquired when an electron is accelerated from rest through a potential difference of 1V; the relation between electronvolts and joules is $1eV \approx 1.6 \times 10^{-19}$ J*

- *Example: the energy to remove an electron from a sodium atom is close to 5 eV*

- *An energy of 1 calorie (cal) is enough to raise the temperature of 1 g of water by 1°C; the relation between calories and joules is $1cal$ = 4.184 J exactly*

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2 Work

- *Expansion Work : the work arising from a change in volume*

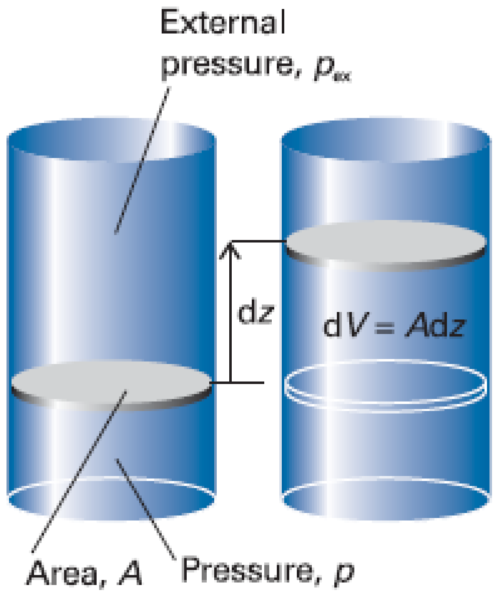
- *Examples: The thermal decomposition of calcium carbonate or the combustion of octane*

$$dw = -Fdz$$

$$F = P_{ex}A$$

$$dw = -P_{ex}Adz$$

$$dw = -P_{ex}dV$$



The negative sign tells us that, when the system moves an object against an opposing force, the internal energy of the system doing the work will decrease

- *To obtain the total work done when the volume changes from V_i to V_f we integrate this expression between the initial and final volumes:*

$$w = -\int_{V_i}^{V_f} P_{external}\, dV$$

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5 Heat Capacity

- *In general, the change in internal energy of a system is*

$$dU = dq + dw_{exp} + dw_e$$

where dw_e is work in addition (e for 'extra') to the expansion work, dw_{exp}

- *If a system is kept at constant volume can do no expansion work, so dw_{exp} = 0 and if it is also incapable of doing any other kind of work, so dw_e = 0.*

- *Under these circumstances(at constant volume, no additional work):*

$$dU = dq_v \text{ or } \Delta U = q_v \text{ (for a measurable change)}$$

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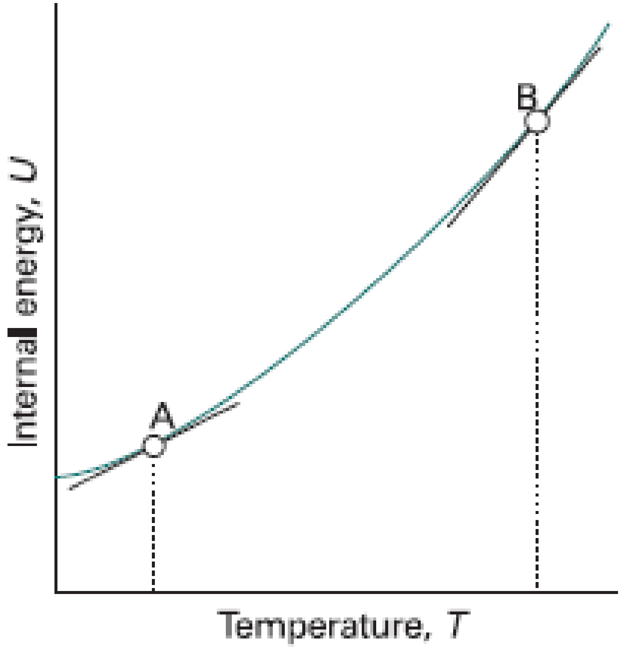
5 Heat Capacity

- *Over small ranges of temperatures, heat capacities can be treated as almost independent of temperature*

- *So, over the range of temperatures of at which the heat capacity is constant, a measurable change of temperature, ΔT, brings about a measurable increase in internal energy, ΔU, where*

$$\Delta U = C_v \Delta T \text{ or } q_v = C_v \Delta T$$



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9 Determining ΔU and Introducing Enthalpy, a New State Function

- *Differentiation of* $H = U + PV$ *leads to*

$$dH = dU + d(PV) \longrightarrow dH = dU + VdP + PdV$$

- *If we now substitute "*$dU = dq + dw$*" into above expression, we get*

$$dH = dq + dw + VdP + PdV$$

- *If the system is in mechanical equilibrium with its surroundings at a pressure P and does only expansion work, we can write dw = −PdV. Also, dP = 0 (why?). So, we obtain*

$$dH = dq - PdV + PdV \longrightarrow dH = dq_p \text{ or } \Delta H = q_p$$

(at constant pressure, no additional work)

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