2.3

Work

From last lecture

"expansion work" or "compression work"

$$dW = -Fdx = -pAdx = pdV$$

$Adx = dV$ → Differential volume change associated with the work done

Specific work

$w = W / m$ → $$dw = -pdv$$

From last lecture

For a finite expansion or compression from v1 to v2:

$$w = -\int_{v_1}^{v_2} p\,dv$$

The work depends on the path, and is not necessarily zero

generally

$$\oint dw \neq 0$$

Work is an algebraic quantity

Positive

Work done **on** a system

Negative

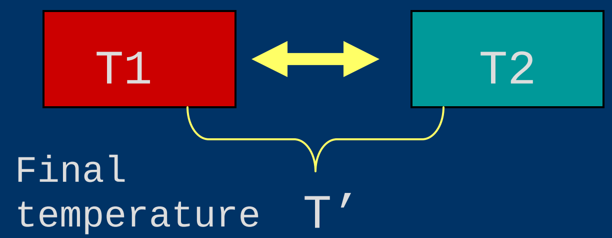
Work done **by** a system

Heat

From last lecture

algebraic quantity

positive when it flows **from the surrounds to the system** (same convention as for work).



The amount of heat lost by the warmer body is equal in magnitude to the amount of the heat gained by the cooler body

$$\Delta Q = c_1 m_1 (T_1 - T') = c_2 m_2 (T' - T_2)$$

<u>Differential form</u>

$$dQ = mcdT$$

First Law of Thermodynamics

Internal energy → U

- Total energy contained in the system
- The internal energy of a system can change only by work or heat exchanges

increment of heat dQ added to a system the energy can be used

- Increase the speed of the molecules
  (Increase temperature of the system)
- To create motion internal to each molecule
  (Rotation and vibration)
- Overcome forces of attraction between molecules
  (Change of state e.g., from liquid to vapor)

The First Law of Thermodynamics is the law of conservation of energy → energy cannot be created or destroyed. Instead it is converted from one form to another mathematical statement

$$\Delta U = U_{final} - U_{initial}$$

Differential form

$$dU = dQ + dW$$

Intensive differential form of the first law

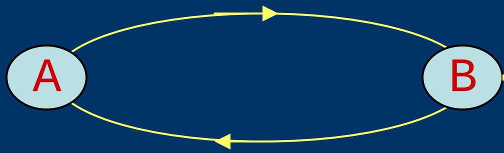
$$du = dq + dw$$

conservation

$$0 = \Delta U_{syst} + \Delta U_{env}$$

Cyclical processes

energy can not be created



$$\Delta U_{syst}(A \rightarrow B \rightarrow A) = \oint du = 0$$

ΔU

Depends only on the initial and final state but not on the path

$$du = dq + dw$$

$$\oint du = 0 \qquad \oint dq \neq 0 \qquad \oint dw \neq 0$$

internal energy form is more convenient for constant volume processes

Constant volume

$$dU = dQ + dW$$

$$dW = -pdV$$

"expansion work" or
"compression work"

$$dU = dQ + pdV$$

$$dV = 0 \quad \Rightarrow \quad \boxed{dU = dQ}$$

Constant pressure and only expansion work

$$\Delta U = U_{final} - U_{initial} = U_2 - U_1$$

$$\Delta U = Q_p + W$$

$$w = -\int_{v_1}^{v_2} pdv$$

$$\Delta U = Q_p - \int_{v_1}^{v_2} pdV$$

$$\Delta U = Q_p - p(V_2 - V_1)$$

$$U_2 - U_1 = Q_p - p(V_2 - V_1)$$

$$(U_2 + pV_2) - (U_1 + p_1V_1) = Q_p$$

$$\underbrace{(U_2 + pV_2)}_{} - (U_1 + p_1V_1) = Q_p$$

H → Enthalpy

$$H = U + pV$$

$$\Delta H = H_2 - H_1 = (U_2 + p_2V_2) - (U_1 + p_1V_1) = Q_p$$

$$dH = dU + pdV + Vdp = dQ + Vdp$$

$$dh = dq + vdp$$

Equivalent forms of the first law

Enthalpy equations

enthalpy form is more convenient for constant pressure process

$$\oint dh = 0$$

$$u = u(p, v, T)$$

$$h = h(p, v, T)$$

u h

State functions

$$u = u(v, T)$$

$$h = h(p, T)$$

$$du = \left(\frac{\partial u}{\partial T}\right) dT + \left(\frac{\partial u}{\partial v}\right) dv \qquad dh = \left(\frac{\partial h}{\partial T}\right) dT + \left(\frac{\partial h}{\partial p}\right) dp$$

Constant volume

$$dv = 0$$

$$du = dq_v$$

$$\rightarrow \quad du = \left(\frac{\partial u}{\partial T}\right) dT = dq_v$$

Constant pressure

$$dp = 0 \quad \rightarrow \quad dh = \left(\frac{\partial h}{\partial T}\right) dT = dq_p$$

Specific heat

$$c = \frac{dq}{dT}$$

$$c_v = \frac{dq_v}{dT} \qquad c_p = \frac{dq_p}{dT}$$

$$du = \left(\frac{\partial u}{\partial T}\right) dT = dq_v \qquad dh = \left(\frac{\partial h}{\partial T}\right) dT = dq_p$$

$$c_v = \frac{dq_v}{dT} = \frac{\partial u}{\partial T} \qquad c_p = \frac{dq_p}{dT} = \frac{\partial h}{\partial T}$$

$$du = \left(\frac{\partial u}{\partial T}\right) dT + \left(\frac{\partial u}{\partial v}\right) dv \qquad dh = \left(\frac{\partial h}{\partial T}\right) dT + \left(\frac{\partial h}{\partial p}\right) dp$$

$$du = c_v dT + \left(\frac{\partial u}{\partial v}\right) dv \qquad dh = c_p dT + \left(\frac{\partial h}{\partial p}\right) dp$$

Ideal Gas

Internal energy is function only of temperature for an ideal gas

$$\left(\frac{\partial u}{\partial v}\right)_T = 0 \qquad \left(\frac{\partial h}{\partial p}\right) = 0$$

$$du = c_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv \qquad dh = c_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp$$

$$du = c_v dT$$

$$dh = c_p dT$$

c_p vs c_v

Constant pressure process

Constant volume process

Some of the added heat

All heat

Doing work on the surroundings

Raising the temperature of the substance

$$c_p > c_v$$

$$c_p - c_v = R$$

"expansion work"

Heat

$$dw = -pdv$$

$$\oint dw \neq 0$$

$$w = -\int_{v_1}^{v_2} pdv$$

$$dQ = mcdT$$

$$\oint dQ \neq 0$$

$$\oint du = 0$$

First Law of Thermodynamics

$$\oint dh = 0$$

$$du = dq + dw$$

$$dh = dq + vdp$$

convenient for constant volume processes

convenient for constant pressure process