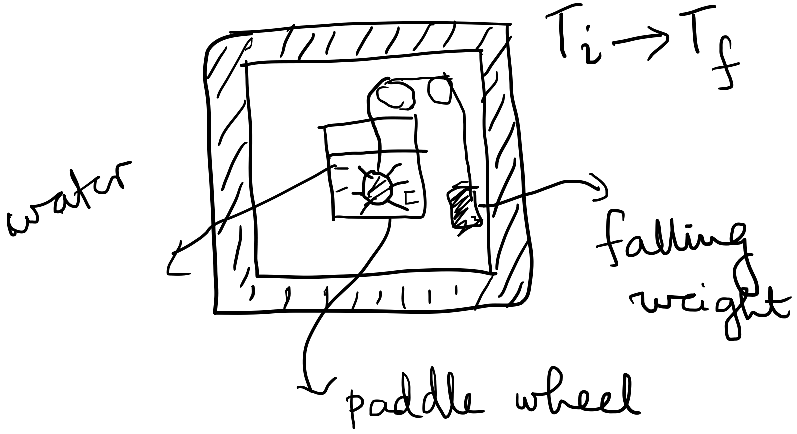
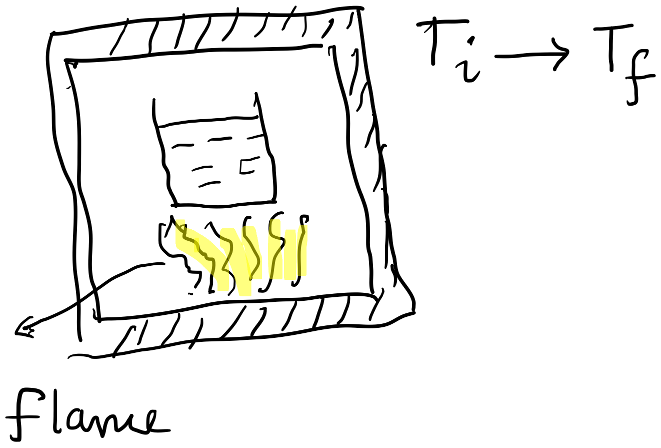
First Law of Thermodynamics

Mechanics: Doing work on an object increases its energy
Conservative systems , E = K + U
Energy: function of dynamical state of the system

Internal energy of a system can be changed in two ways
- Doing work on the system

Adding heat to the system (putting it in contact with a hotter body)





- There exists a state function $U(X, Y)$ that represents the internal energy of the thermodynamic system with coordinates X, Y.

e.g , for P VT system $U(P, V)$ or $U(P, T)$ or $U(V, T)$

In most cases the precise form of the internal energy function not known. The first law guarantees that it exists.

(Microscopically, = sum of kinetic and potential energies of the constituent particles)

$$\boxed{U(B) - U(A) = W(A \to B) + Q(A \to B)} \quad (1)$$

1st Law

heat absorbed > 0

$$\boxed{dU = đW + đQ} \quad (2)$$

$$\int_A^B dU = U(B) - U(A) \longrightarrow \text{path ind}$$

Heat Capacity

Adding heat → raises temp

$$\boxed{C_v = \left(\frac{đQ}{dT}\right)_v \quad ; \quad C_p = \left(\frac{đQ}{dT}\right)_p} > 0$$

$$Q(A \to B) = \int_{T_A}^{T_B} C_v \, dT \qquad \text{const } V$$

$$Q(A \to B) = \int_{T_A}^{T_B} C_p \, dT \qquad \text{Const } P$$

$C_V(T)$, $C_P(T)$ ⇝ expt'ly determined

$$c_V = \frac{C_V}{n}, \quad c_P = \frac{C_P}{n} \longrightarrow \text{molar heat capacities.}$$

$C_P, C_P \longrightarrow \infty$ reservoirs

Some formal manipulations

$U(V,T)$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \quad \text{— (1)}$$

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$$\left.\begin{aligned} dU &= đQ + đW \\ đW &= -p\,dV \end{aligned}\right\}$$

$$đQ = dU + p\,dV \quad \text{— (2)}$$

$$= \left(\frac{\partial U}{\partial V}\right)_T dV + p\,dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$V = \text{const.}$

$$\boxed{\left(\frac{đQ}{dT}\right)_V = C_V = \left(\frac{\partial U}{\partial T}\right)_V}$$

$\underline{\underline{C_p}}$

$$U(P,T)$$

$$dU = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT$$

$$\text{đ}Q = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT + p\,dV$$

$$V(T,P) \rightarrow dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

$$\text{đ}Q = \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP + \left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT$$

$$\boxed{C_p = \left(\frac{\text{đ}Q}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P} \leftarrow 4$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$, define $H = U + PV$

can check $C_P = \left(\frac{\partial H}{\partial T}\right)_P$.

Relationship between C_p & C_v

$$đQ = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV + \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_v} dT$$

$$đQ = C_v\, dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV$$

$$\left(\frac{đQ}{dT}\right)_P = C_v + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$\boxed{C_p = C_v + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \beta V}$$

for an ideal gas
U is independent of V (from kinetic theory)

$$C_p = C_v + P\beta V$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$V = \frac{nRT}{P}.$$

$$V\beta = \frac{nR}{P}.$$

$$C_p - C_v = nR$$