Definitions

Isolated system: No exchanges

Closed system: Only energy exchange

Open system: Energy & mass exchange

Intensive state variables:
Independent of mass

Extensive state variables:
Proportional to mass

Reservoirs: Infinite/very large system that remains unchanged when in contact with finite system.

Mechanical equilibrium:
No unbalanced forces

Thermal equilibrium:
No temperature differences

Thermodynamic equilibrium:
Intensive state variables of system are constant. Alternatively our system is in mechanical and thermal equilibrium.

Reversible processes:
Every intermediate is an equilibrium state.

Quasi-static processes:
Process sufficiently slow such that only infinitesimal temperature or pressure gradients exist.

Frictionless quasi-static processes are reversible.

Cyclic processes:

$$\oint \mathrm{d}X = 0$$

where X is a state variable.

Zeroth law

If A is in thermal equilibrium with B and C seperately then B and C are also in thermal equilibrium.

Ideal gas state equation

Given n moles of gas at temperature T:

$$PV = nRT$$

where $R = 8.314\mathrm{JK}^{-1}\mathrm{mol}^{-1}$.

First law

$$\mathrm{d}U = \mathrm{d}Q - \mathrm{d}W$$

Note $Q > 0$ represents energy transferred into system. When system does work on surroundings $W > 0$.

Work done by fluid in reversible process:

$$\mathrm{d}W = P\mathrm{d}V.$$

Isochoric heat capacity

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

Isobaric heat capacity

$$\begin{aligned} C_P &= \left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_P \\ &= C_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \end{aligned}$$

Heat capacity has units JK^{-1}.

For ideal gases:

$$C_P - C_V = nR$$

$$TV^{\gamma-1} = \text{constant}$$

$$\gamma = \frac{C_P}{C_V}.$$

State function enthalpy

$$H = U + PV$$

$$\begin{aligned} \mathrm{d}H &= \mathrm{d}U + V\mathrm{d}P + P\mathrm{d}V \\ &= \mathrm{d}Q + V\mathrm{d}P \end{aligned}$$

$$\therefore C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

Chemical reactions

$$Q = \Delta U + P_0\Delta V = \Delta H$$

Here P_0 is constant.

- $Q < 0$: exothermic
  (heat is released)
- $Q > 0$: endothermic
  (heat is absorbed)

Carnot's theorem

Peak efficiency of a cyclic heat engine:

$$\eta = 1 - \frac{Q_C}{Q_H}.$$

State function entropy

$$S = \frac{Q}{T}$$

For reversible cyclic heat engine:

$$\mathrm{d}S = \frac{\mathrm{d}Q}{T}.$$

$$\therefore \mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$$