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:

$$\Delta U = 0 \text{ and } W = Q$$

For conservative forces:

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

where X is a state variable.

Adiabatic processes: $\Delta Q = 0$

Isothermal processes: $\Delta T = 0$

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

Total energy E is conserved and:

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

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

Work done by fluid in reversible adiabatic processes:

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

and is in Joules (J).

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 we have that:

$$C_P - C_V = nR.$$

Under reversible adiabatic processes:

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

$$PV^{\gamma} = \text{constant}$$

$$T^{\frac{1}{\gamma-1}}V = \text{constant}$$

where γ is the adiabatic exponent:

$$U = \frac{f}{2}nRT$$

$$\gamma = \frac{C_P}{C_V} = \frac{f+2}{f}$$

regardless of degrees of freedom f.

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:

$$\eta = \frac{\dot{W}}{\dot{Q}_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

and is either in terms of rate or value, with units J or Js^{-1}.

State function entropy

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

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

Entropy of mixing

$$\Delta S = n_A R \ln\frac{V_A + V_B}{V_A} + n_B R \ln\frac{V_A + V_B}{V_B}$$

$$\Delta s_{mix} = -R(x_A \ln x_A + x_B \ln x_B)$$

$$x_A = \frac{n_A}{n_A + n_B} \text{ and } x_B = \frac{n_B}{n_A + n_B}$$

Second law

$$\Delta S_{total} = \Delta_{system} + \Delta_{reservoir} \geq 0$$

$$\mathrm{d}S \geq \frac{\mathrm{d}Q}{T}$$

Helmholtz free energy

$$F = U - TS$$

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

Gibbs free energy

$$G = H - TS$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P$$

Chemical reactions are spontaneous if:

$$\Delta G = \Delta H - T\Delta S < 0.$$

Maxwell relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

The isobaric expansivity is defined as:

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

and the isothermal compressibility:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T.$$

Clausius-Clapeyron equation

The slope of any phase boundaries is:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta S}{\Delta V}.$$

Van der Waals state equation

$$\left(P + \frac{an^2}{V^2}\right)\left(V - nb\right) = nRT$$

Chemical potentials

$$\mu = \frac{G}{N}$$

Third law

$S = 0$ at $T = 0\mathrm{K}$.