## 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:

$$\oint dX = 0$$

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 $T$:

$$PV = nRT$$
$$= Nk_BT$$

where $R = N_Ak_B = 8.314\text{JK}^{-1}\text{mol}^{-1}$ and $N$ the number of molecules.

## Calculus identities

1. $\left(\dfrac{\partial Z}{\partial Y}\right)_X = \left[\left(\dfrac{\partial Y}{\partial Z}\right)_X\right]^{-1}$

2. $\left(\dfrac{\partial X}{\partial Y}\right)_Z\left(\dfrac{\partial Y}{\partial Z}\right)_X\left(\dfrac{\partial Z}{\partial X}\right)_Y = -1$

## First law

Total energy $E$ is conserved and:

$$\Delta U = Q - W$$

$$dU = dQ - dW$$

$$\dot{U} = \dot{Q} - \dot{W}$$

where $U$ is internal energy and $E \geq U$.

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

Work done by a fluid in reversible adiabatic processes:

$$dW = PdV$$

and is in Joules (J).

## Isochoric heat capacity

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

## Isobaric heat capacity

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

Heat capacity has units $\text{JK}^{-1}$.

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 $\gamma$ 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

$$H = U + PV$$

$$dH = dU + VdP + PdV$$
$$= dQ + VdP$$

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

Enthalpy has units $J$.

## Latent heats

Latent heat is heat needed for sample to undergo a phase transition:

$$\Delta U_{m,V} = Q_{m,V} - P\Delta V_{m,V}$$

$$Q_{m,V} = \Delta H_{m,V}.$$

## Chemical reactions

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

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

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

at constant pressure $P_0$.

## 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 $\text{Js}^{-1}$.

## Entropy

The state function entropy is a measure of disorder defined as:

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

where $Q$ is heat received from a reservoir at temperature $T$ and units $\text{JK}^{-1}$.

$$\therefore dU = TdS - PdV$$

$$\therefore dH = dQ + VdP$$

## Entropy of mixing

$$\Delta S = n_AR\ln\frac{V_A+V_B}{V_A} + n_BR\ln\frac{V_A+V_B}{V_B}$$

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

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

## Second law

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

$$dS \geq \frac{dQ}{T}$$

**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**

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

**Chemical potentials**

The Euler equation for a 1-component **open** system with $N$ particles is:

$$U = TS - PV + \mu N$$

with modified first law statement:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N.$$

This gives the Gibbs-Duhem relation:

$$S\mathrm{d}T - V\mathrm{d}P + N\mathrm{d}\mu = 0$$

where $\mu$ is the chemical potential:

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

since $G$ is extensive. At constant $T$ with ideal gas assumptions:

$$\mu(P, T) = RT \ln \frac{P}{P_0} + \mu_0.$$

**Third law**

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