

## 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:**  $\Delta T = 0$

**Isobaric processes:**  $\Delta P = 0$

**Zeroth law**

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

**Ideal gas state equation**

Given  $n$  moles of gas at temperature  $T$ :

$$PV = nRT$$

$$= Nk_B T$$

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

## Calculus identities

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

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

## 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  $f$ .

## Enthalpy

The state function enthalpy simplifies the description of heat transfer.

Enthalpy has units J and is defined as:

$$H = U + PV$$

$$dH = dU + VdP + PdV$$

$$= dQ + VdP.$$

Under isobaric reversible conditions:

$$dH = dQ_P.$$

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

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

Then for a reversible cyclic heat engine:

$$dU = TdS - PdV.$$

For all processes the following holds:

$$dH = dQ + VdP.$$

## 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**

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

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

**Helmholtz free energy**

$$F = U - TS$$

$$dF = -SdT - PdV$$

**Gibbs free energy**

$$G = H - TS$$

$$dG = -SdT + VdP$$

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:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}.$$

**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:

$$dU = TdS - PdV + \mu dN.$$

This gives the Gibbs-Duhem relation:

$$SdT - VdP + Nd\mu = 0$$

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  $T = 0\text{K}$ .