

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

## Density

We define the density of a material as:

$$\rho = \frac{m}{V}.$$

If mass  $m$  is constant:

$$\Delta V = m \left( \frac{1}{\rho_f} - \frac{1}{\rho_i} \right)$$

assuming homogeneous material.

## 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  $T$ :

$$\begin{aligned} PV &= nRT \\ &= Nk_B T \end{aligned}$$

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

## Calculus identities

$$1. \quad df(x, y) = \left( \frac{\partial f}{\partial x} \right)_y dx + \left( \frac{\partial f}{\partial y} \right)_x dy$$

if  $f = f(x, y)$ .

2. Differential  $df$  is **inexact** if:

$$\int_C df \text{ is } \underline{\text{dependent}} \text{ of path.}$$

$$3. \quad \left( \frac{\partial Z}{\partial Y} \right)_X = \left[ \left( \frac{\partial Y}{\partial Z} \right)_X \right]^{-1}$$

$$4. \quad \left( \frac{\partial X}{\partial Y} \right)_Z \left( \frac{\partial Y}{\partial Z} \right)_X \left( \frac{\partial Z}{\partial X} \right)_Y = -1$$

## 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  $E \geq U$ .

- Heat exchange  $Q$ :

The energy transfer of two systems at different temperatures in thermal contact.  $Q > 0$  represents energy transfer into system.

- Work exchange  $W$ :

The work done on the surroundings by system is represented by  $W > 0$ .

Work is generally path dependent.

The work done by a fluid in **reversible** processes is:

$$dW = PdV$$

and has units Joules (J).

## Isothermal expansion

Let  $P_1 > P_2$  where  $P_1$  and  $P_2$  denote system and external pressure respectively. Only mechanical work is exchanged via a piston. By applying a force such that there exists pressure difference  $dP$ , our expansion becomes reversible and hence:

$$W_{1 \rightarrow 2} = nRT \int_{V_1}^{V_2} \frac{dV}{V}.$$

Note that for isothermal processes under ideal gas assumption,  $\Delta U = 0$ .

## Heat capacity

Heat capacity ( $\text{JK}^{-1}$ ) is defined as:

$$C(P, T) = \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T}$$

and is the heat needed to produce unit change in sample temperature.

Specific heat capacity ( $\text{Jkg}^{-1} \text{K}^{-1}$ ):

$$Q = mc\Delta T.$$

We define the **isochoric** heat capacity as:

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

and the **isobaric** heat capacity as:

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

For ideal gases we have that:

$$C_P - C_V = nR.$$

## Adiabatic expansion

The reversible adiabatic expansion of an **ideal** gas is given by:

$$\begin{aligned} dU &= -PdV \text{ and } dU = C_V dT \\ \Rightarrow \frac{dT}{T} + \frac{C_P - C_V}{C_V} \frac{dV}{V} &= 0 \end{aligned}$$

since  $U = U(T)$ . Integrating this yields:

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

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

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

where  $\gamma$  is the adiabatic exponent:

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

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

and  $f$  is degrees of freedom. The practical computation of work done for adiabats is given by:

$$W_{1 \rightarrow 2} = - \int_{T_1}^{T_2} C_V dT.$$

## General form for first law

Given system with  $m$  conjugate pairs  $(x_i, X_i)$  that represent various modes of work exchange:

$$dU = dQ + \sum_{i=1}^m x_i dX_i$$

for each  $\{x_i\}$  drives  $\{X_i\}$ .

## Enthalpy

The state function enthalpy simplifies the description of heat transfer.

Enthalpy has units J and is defined as:

$$H = U + PV$$

$$\begin{aligned} dH &= dU + VdP + PdV \\ &= dQ + VdP. \end{aligned}$$

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:

$$\Delta U_m = Q_m - P\Delta V_m$$

$$L_m = Q_m = \Delta H_m.$$

## Chemical reactions

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

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

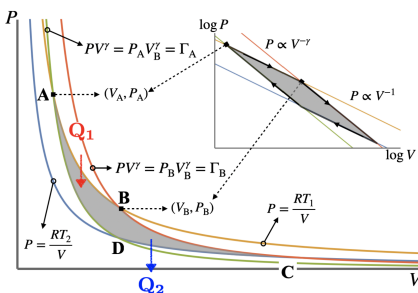
at constant pressure  $P_0$ .

## Carnot's theorem

Peak efficiency of a cyclic heat engine:

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

and is either in terms of rate or value, with units J or Js<sup>-1</sup>. This ideal cycle is known as the Carnot cycle:



where AB, CD are isothermal processes and BC, DA are adiabatic processes.

## 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 JK<sup>-1</sup>.

Then for a reversible cyclic heat engine:

$$dS = dQ/T$$

$$dU = TdS - PdV.$$

For all processes the following holds:

$$dH = TdS + VdP.$$

## 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

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

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

## 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:

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

## Throttling

Throttling is the adiabatic reduction in gas pressure and is an isenthalpic process. We define the slope of a P-T plot:

$$\begin{aligned} \mu_{JK} &= \left( \frac{\partial T}{\partial P} \right)_H \\ &= \frac{V(T, P)}{C_P} (\beta T - 1) \end{aligned}$$

as the Joule-Kelvin coefficient.

## Clausius-Clapeyron equation

The slope of any phase boundary is:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}$$

since constant pressure at boundaries.

## 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:

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

Chemical potential  $\mu$  has units J.

## Third law

$S = 0$  at  $T = 0K$ .

## Questions

1. What is temperature?