

## 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:

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

Generally  $C_P > C_V$  and for ideal gases:

$$C_P - C_V = nR.$$

## 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:

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

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

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

where  $\gamma$  is the adiabatic exponent:

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

$$U = \frac{f}{2} nRT \Rightarrow C_V = \frac{f}{2} nR$$

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:

$$H = U + PV.$$

Under reversible conditions:

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

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

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

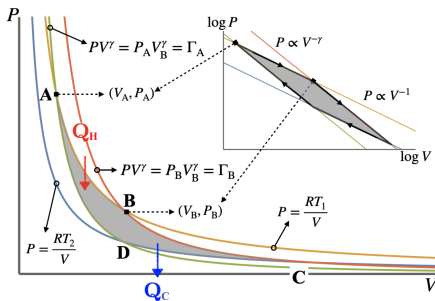
$$\Delta U = Q_\ell - P\Delta V \implies Q_\ell = \Delta H.$$

## Carnot's theorem

Peak efficiency of a cyclic heat engine:

$$\begin{aligned} \eta &:= \frac{W}{Q_H} = \frac{\dot{W}}{\dot{Q}_H} \\ &= 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H} \end{aligned}$$

since  $\Delta U = 0 \implies W = Q = Q_H - Q_C$ . This is 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  $\text{JK}^{-1}$ .

Under reversible processes:

$$\Delta S_{1 \rightarrow 2} = \int_{T_1}^{T_2} \frac{dQ}{T}$$

$$\therefore dQ_{rev} = 0 \implies dS = 0$$

$$dU = TdS - PdV$$

$$dH = TdS + VdP.$$

## Entropy of ideal gases

The internal energy of an ideal gas is  $dU = C_V dT$  and from first law:

$$dS = C_V \frac{dT}{T} + nR \frac{dV}{V}.$$

Integrating yields the change in entropy:

$$\begin{aligned} \Delta S(V, T) &= C_V \ln \frac{T}{T_0} + nR \ln \frac{V}{V_0} \\ \implies S &= \Delta S + S_0 \end{aligned}$$

given change in state  $(V_0, T_0) \rightarrow (V, T)$ .

## Entropy of mixing

For ideal gases A and B:

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

The molar specific entropy of mixing is:

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

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

## Second law

Total entropy cannot decrease:

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

due to the Clausius inequality:

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

and generally  $dS = 0 \not\Rightarrow dQ = 0$ .

$$\therefore W_{rev} - W_{irr} = T\Delta S_{irr} > 0$$

## Helmholtz free energy

$$F = U - TS$$

For reversible processes:

$$dF = -SdT - PdV.$$

## Gibbs free energy

$$G = H - TS$$

For reversible processes:

$$dG = -SdT + VdP.$$

## 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  $P_0$ .

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:

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

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

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

A good approximate state equation for non-ideal gases is:

$$\left( P + \frac{a}{v^2} \right) (v - b) = RT$$

with **molar volume**  $v := V/n$ .

$a/v^2$  accounts for molecular interactions and  $b$  the finite volume of molecules.

**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  $T = 0\text{K}$ .

**Questions**

1. What is temperature?