

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 (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 γ 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:

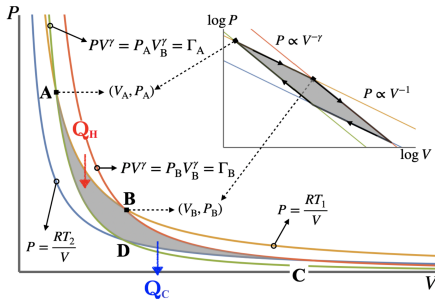
$$\Delta U = Q_\ell - P\Delta V \implies Q_\ell = \Delta H.$$

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 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

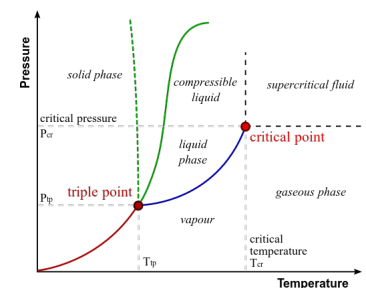
A good approximate state equation for non-ideal gases is:

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

with **molar volume** $v := V/n$. The term a/v^2 accounts for **molecular interactions** and term b the **finite volume** of molecules.

At the **critical point** $(\partial P/\partial v)_T = 0$ and $(\partial^2 P/\partial v^2)_T = 0$ which gives:

$$P_c = \frac{a}{27b^2}, \quad T_c = \frac{8a}{27bR} \text{ and } v_c = 3b.$$



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 μ 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 μ has units J.

Third law

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

Questions

1. What is temperature?