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:

$$\oint \mathrm{d}X = 0$$

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 seperately then B and C are also in thermal equilibrium.

Ideal gas state equation

Given n moles of gas at temperature T:

$$\begin{aligned} PV &= nRT \\ &= Nk_BT \end{aligned}$$

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

Calculus identities

1. $\mathrm{d}f(x,y) = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}x$ if $f = f(x,y)$.
2. $\left(\frac{\partial Z}{\partial Y}\right)_X = \left[\left(\frac{\partial Y}{\partial Z}\right)_X\right]^{-1}$
3. $\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X \left(\frac{\partial Z}{\partial X}\right)_Y = -1$

First law

Total energy E is conserved and:

$$\Delta U = Q - W$$

$$\mathrm{d}U = đQ - đW$$

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

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 $W > 0$.

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

$$đW = P\mathrm{d}V$$

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 $\mathrm{d}P$, our expansion becomes reversible and hence:

$$W_{1\to 2} = nRT\int_{V_1}^{V_2} \frac{\mathrm{d}V}{V}.$$

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

Heat capacity

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

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

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:

$$C_V(T) := \left(\frac{đQ}{\mathrm{d}T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

and the **isobaric** heat capacity as:

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

For ideal gases we have that:

$$C_P - C_V = nR.$$

Adiabatic expansion

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

$$\begin{aligned} &\mathrm{d}U = -P\mathrm{d}V \text{ and } \mathrm{d}U = C_V\mathrm{d}T \\ \implies &\frac{\mathrm{d}T}{T} + \frac{C_P - C_V}{C_V}\frac{\mathrm{d}V}{V} = 0 \end{aligned}$$

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 γ 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:

$$W_{1\to 2} = -\int_{T_1}^{T_2} C_V\mathrm{d}T.$$

Enthalpy

The state function enthalpy simplies the description of heat transfer.

Enthalpy has units J and is defined as:

$$H = U + PV$$

$$\begin{aligned} \mathrm{d}H &= \mathrm{d}U + V\mathrm{d}P + P\mathrm{d}V \\ &= \mathrm{d}Q + V\mathrm{d}P. \end{aligned}$$

Under isobaric reversible conditions:

$$\mathrm{d}H = \mathrm{d}Q_P.$$

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

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.

General form for first law

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

$$\mathrm{d}U = \mathrm{d}Q + \sum_{i=1}^{m} x_i \mathrm{d}X_i$$

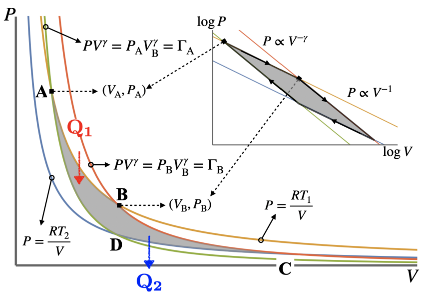
for each generalised force $\{x_i\}$ drives generalised differential displacement $\{X_i\}$.

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 Js^{-1}. 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^{-1}.

Then for a reversible cyclic heat engine:

$$\mathrm{d}S = \mathrm{d}Q/T$$

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

For all processes the following holds:

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P.$$

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

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

$$\mathrm{d}S \geq \frac{\mathrm{d}Q}{T}$$

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:

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

Throttling

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

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

as the Joule-Kelvin coefficient.

Clausius-Clapeyron equation

The slope of any phase boundary is:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}$$

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:

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

This gives the Gibbs-Duhem relation:

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

where 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 $T = 0\mathrm{K}$.

Questions

1. What is temperature?