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 <u>constant</u>. Alternatively our system is in <u>mechanical</u> and <u>thermal</u> 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 <u>reversible</u>.

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 <u>seperately</u> then B and C are also in thermal equilibrium.

Ideal gas state equation

Given n moles of gas at temperature T:

$$PV = nRT$$
$$= Nk_BT$$

where $R = N_A k_B = 8.314 \mathrm{JK}^{-1}\mathrm{mol}^{-1}$ 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. Differential $\mathrm{d}f$ is **inexact** if:

   $$\int_C \mathrm{d}f \text{ is } \underline{\text{dependent}} \text{ of path.}$$

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

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

First law

Total energy E is conserved and:

$$\Delta U = Q - W$$
$$\mathrm{d}U = \mathrm{d}Q - \mathrm{d}W$$
$$\dot{U} = \dot{Q} - \dot{W}$$

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 <u>into</u> system.

- Work exchange W:
  The work done <u>on</u> the surroundings by system is represented by $W > 0$.

  Work is generally <u>path dependent</u>.

The work done <u>by</u> a fluid in **reversible** processes is:

$$\mathrm{d}W = P\mathrm{d}V$$

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 <u>ideal</u> 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 $(\mathrm{Jkg}^{-1}\mathrm{K}^{-1})$:

$$Q = mc\Delta T.$$

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

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

and the **isobaric** heat capacity as:

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

For ideal gases we have that:

$$C_P - C_V = nR.$$

Adiabatic expansion

The <u>reversible</u> <u>adiabatic</u> expansion of an **ideal** gas is given by:

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

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 <u>adiabatic exponent</u>:

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

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

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

General form for first law

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

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

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

Enthalpy

The state function enthalpy simplies the description of heat transfer.

Enthalpy has units J and is defined as:

$$H = U + PV.$$

Under reversible conditions:

$$\mathrm{d}H = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P$$
$$= \mathrm{d}Q + V\mathrm{d}P$$

$$\therefore \mathrm{d}H = \mathrm{d}Q_P \implies C_P = \left(\frac{\partial H}{\partial T}\right)_P.$$

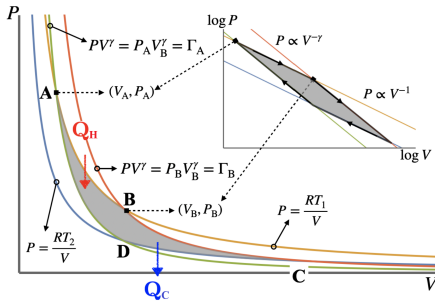Latent heat (J) is heat needed for sample to undergo a phase transition:

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

Carnot's theorem

Peak efficiency of a cyclic heat engine:

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

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}.

For reversible processes:

$$\Delta S_{1\to2} = \int_{T_1}^{T_2} \frac{\mathrm{d}Q}{T}$$

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

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

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:

$$\mathrm{d}S \geq \frac{\mathrm{d}Q}{T}.$$
$$\therefore W_{rev} - W_{irr} = T\Delta S_{irr} > 0$$

Helmholtz free energy

$$F = U - TS$$

For reversible processes:

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

Gibbs free energy

$$G = H - TS$$

For reversible processes:

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

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:

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

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 $T = 0$K.

Questions

1. What is temperature?