0.1 Review on Thermodynamics

0.1.1 System, Surroundings and Boundary

Thermodynamic system - An amount of matter "or" a region of space chosen for study
Surroundings - The region of space outside the arbitrary System boundary
Boundary - surface that separates the system from surrounding:

- Real or imaginary
- Massless
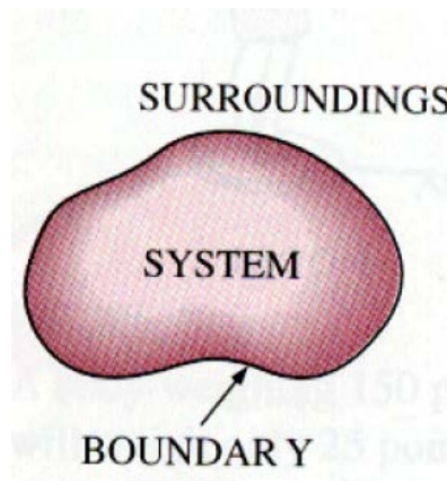- Fixed (rigid tank) or movable (piston), flexible (balloon)

Figure 1:

Identification of system and its surroundings is the most critical first step to begin thermodynamic analysis.

0.1.2 System Classifications

Different types of systems can be found, depending on whether work, heat or mass cross the system boundary.

Definition		Work	Heat	Mass
Isolated System		No	No	No
Closed System	(Control Mass)	Yes	Yes	No
Open System	(Control Volume)	Yes	Yes	Yes

0.1.3 Thermodynamic Properties - Extensive vs. Intensive

Extensive properties are additive (i.e. depending on size/mass of system)

- U: internal energy [kJ]
- H: enthalpy [kJ]

- S: entropy [kJ/K]
- V: volume [m³]

Intensive properties are non-additive (i.e. independent of size/mass of system)

- T: temperature [K]
- h: specific enthalpy [kJ/kg]
- P: pressure [Pa]
- s: specific entropy [kJ/(kg K)]
- x: quality [-]
- v: specific volume [m³/kg]
- u: specific internal energy [kJ/kg]
- ρ: density [kg/m³]

Extensive properties per unit mass or mole are called specific properties, which become intensive properties.

0.1.4   State, Equilibrium State, Steady State

State of a system is the condition characterized by a given set of properties, as well as their distributions in space. For a simple system of pure homogeneous substance, the state is uniquely specified by just two properties such as T and P or V and S.

Thermodynamic equilibrium (state) implies that a system state cannot change in the absence of unbalanced driving **forces"** between the system and surroundings. It requires the following equilibrium within the system:

- Thermal equilibrium (constant temperature)
- Mechanical equilibrium (no pressure difference without gravity)
- Chemical equilibrium (no chemical reactions)
- Phase equilibrium (no phase change)

Steady state requires none of its properties changes with time, but within the system, the properties at different locations can be different.

0.2   Ideal Gas

Ideal gas is an imaginary substance whose properties satisfy the following state equation:

$$PV = nRT \tag{1}$$

Some Assumptions:

- No molecular volume: molecules do not occupy space
- No intermolecular forces: intermolecular force can be neglected

These assumptions are not always valid. Substances may be treated as ideal gases for engineering applications at sufficiently low pressure and high temperatures (i.e. low density)

0.2.1 Ideal Gas Equation of State

On a molar basis:

$$PV = NR_uT \qquad (2)$$

$$P\overline{v} = R_uT \qquad (3)$$

On a mass basis:

$$PV = mRT \qquad (4)$$

$$Pv = RT \qquad (5)$$

Where:

- N = number of moles of gas [kmol]
- T = absolute temperature [K]
- R_u = universal gas constant = 8.314 [$\text{kJ kmol}^{-1}\text{K}^{-1}$]
- V = volume [m^3]
- v = specific volume [m^3kg^{-1}]; $\overline{v}$ [$\text{m}^3\text{kmol}^{-1}$]
- $R = R_u/M$ = specific gas constant [kJ/kgK]
- M = molecular weight of gas [kg/kmol]

0.2.2 Limitations on Ideal Gas EoS

- Usually good for air, N_2, O_2, H_2, He, Ar, Ne at low pressures and high temperatures (less than 1% error)

- Works well for water vapour below 10kPa irrespective of temperature (less than 0.1% error)

- Fails close to critical point and saturated vapour line

- Definitely not applicable for water vapour in steam power plants owing to very high pressures

0.3 Ideal Gas Mixtures

Aim: To develop rules for evaluating the properties of gas mixtures using the properties of individual gases (called components or constituents).

Assumptions:

- Each gas in the mixture behaves like an ideal gas.
- The overall mixture behaves like an ideal gas.

Examples:

- Air
- Syngas
- Exhaust gases of a combustion process

0.4 Composition of Mixtures

State of a mixture is fully determined by:

- Composition: mass m_i or number of moles n_1 of each component;

- Two independent intensive properties (such as p and T or v and T).

Mass m_i, number of moles n_i and molecular weight M_i of each component i are related by:

$$n_i = \frac{m_i}{M_i} \tag{6}$$

Mass fraction, x_i:

$$x_i = \frac{m_i}{m} \longrightarrow \sum_{i=1}^{k} x_i = 1 \tag{7}$$

$$\text{Mass fraction based analysis} \longrightarrow \text{gravimetric analysis}$$

Mole fraction, y_i:

$$y_i = \frac{n_i}{n} \longrightarrow \sum_{i=1}^{k} y_i = 1 \tag{8}$$

$$\text{Molar analysis} \longrightarrow \text{volumetric analysis}$$

Apparent or Average molecular weight, M:

$$M = \frac{m}{n} = \frac{\sum_{i=1}^{k} m_i}{n} = \frac{\sum_{i=1}^{k} n_i M_i}{n} = \sum_{i=1}^{k} y_i M_i \tag{9}$$

Total mass of the mixture:

$$m = m_1 + m_2 + \cdots + m_k = \sum_{i=1}^{k} m_i \tag{10}$$

Mass fraction of ith component:

$$x_i = \frac{m_i}{m} \longrightarrow \sum_{i=1}^{k} x_i = 1 \tag{11}$$

Total number of moles:

$$n = n_1 + n_2 + \cdots + n_k = \sum_{i=1}^{k} n_i \tag{12}$$

Mole fraction of ith component:

$$y_i = \frac{n_i}{n} \longrightarrow \sum_{i=1}^{k} y_i = 1 \tag{13}$$

Molar mass:

$$M_i = \frac{m_i}{n_i} \text{ (single component)} \qquad M = \frac{m}{n} \text{ (mixture)} \tag{14}$$

$$m = n_1 M_1 + n_2 M_2 + \cdots + n_k M_k = nM \tag{15}$$

0.4.1   Composition of Air

In practical calculations, air can be assumed to consist of 21% oxygen and 79% nitrogen by volume.

Constituent	Mass Fraction x_i	Molar Mass M_i	Moles n_i per kg of mixture	Mole Fraction y_i
O_2	0.232	32	0.00725	0.210
N_2	0.756	28.01	0.02699	0.781
Ar	0.012	39.94	0.00300	0.009
Air	1	28.96 kg kmol^{-1}	0.03454 kmol/kg$_{air}$	1.0

$$M_{air} = \frac{m_{air}}{n_{air}} = \frac{1}{0.03454} = 28.96 \text{kg kmol}^{-1} \tag{16}$$

0.5   P-v-T Relationships of Ideal Gas Mixtures
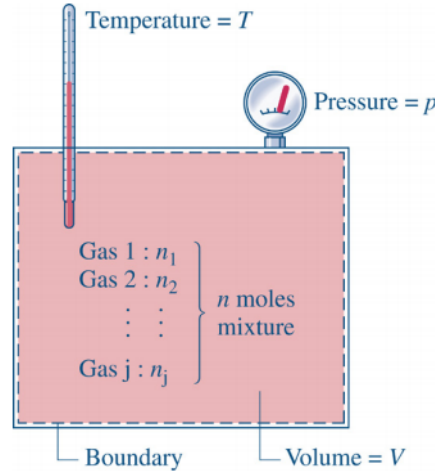
0.5.1   Dalton's Law

Figure 2:

The pressure of a gas mixture is equal to the sum of the pressures each gas would exert if it existed alone at the mixture temperature and volume.
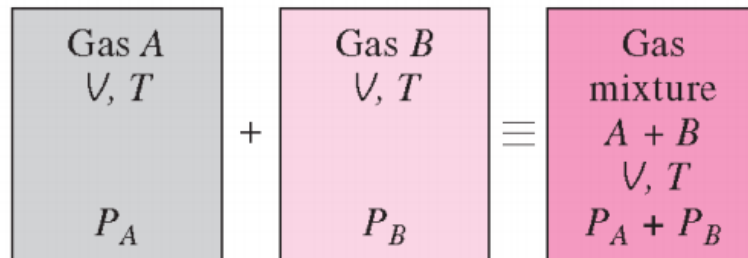

Figure 3:

Ideal gas law and the universal gas constant are, respectively:

$$p_i V = n_i \overline{R} T \tag{17}$$

$$\overline{R} = R_u = R_0 = 8.314 \text{kJ kmol}^{-1} \text{K}^{-1} \tag{18}$$

The pressure of each component occupying the whole volume of the mixture at the same mixture temperature is a **partial pressure**:

$$p_i = \frac{n_i \overline{R} T}{V} \tag{19}$$

$$p = \frac{n \overline{R} T}{V} \tag{20}$$

$$\frac{p_i}{p} = \frac{n_i}{n} = y_i \tag{21}$$

$$p_i = y_i p \tag{22}$$

$$\sum_{i=1}^{j} p_i = \sum_{i=1}^{j} y_i p = p \sum_{i=1}^{j} y_i = p \tag{23}$$
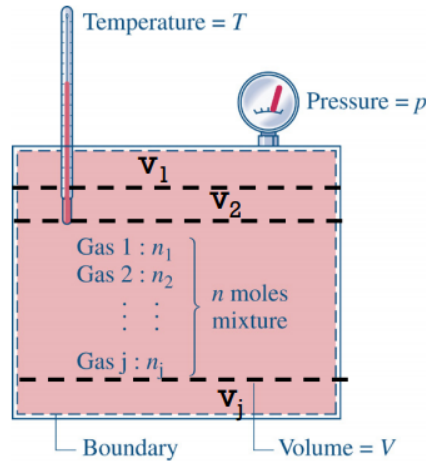
0.5.2 Amagat's Law

Figure 4:

The volume of a gas mixture is equal to the sum of the volumes each gas would occupy if it existed alone at the mixture temperature and pressure.
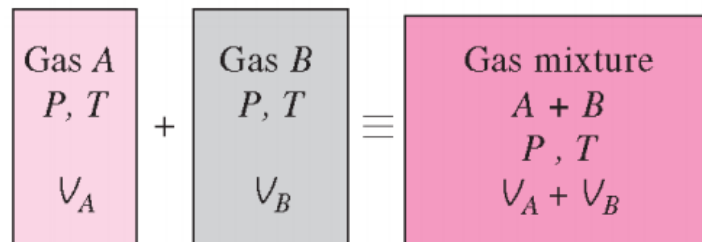

Figure 5:

Ideal gas law and the universal gas constant are, respectively:

$$pV_i = n_i \overline{R} T \tag{24}$$

$$\overline{R} = R_u = R_0 = 8.314 \text{kJ kmol}^{-1} \text{K}^{-1} \tag{25}$$

The volume occupied by each component at the same pressure p and temperature T of the mixture is a **partial volume**:

$$V_i = \frac{n_i \overline{R} T}{p} \tag{26}$$

$$V = \frac{n \overline{R} T}{p} \tag{27}$$

$$\frac{V_i}{V} = \frac{n_i}{n} = y_i \tag{28}$$

$$V_i = y_i V \tag{29}$$

$$\sum_{i=1}^{j} V_i = \sum_{i=1}^{j} y_i V = V \sum_{i=1}^{j} y_i = V \tag{30}$$

0.6   Properties of Ideal Gas Mixtures

Extensive properties U, H, S and intensive properties u, h, s:

Internal Energy

$$U = U_1 + U_2 + \cdots + U_k = \sum_{i=1}^{k} U_i \tag{31}$$

$$U = m_1 u_1 + m_2 u_2 + \cdots + m_k u_k = \sum_{i=1}^{k} m_i u_i = mu \tag{32}$$

$$U = n_1 \overline{u_1} + n_2 \overline{u_2} + \cdots + n_k \overline{u_k} = \sum_{i=1}^{k} n_i \overline{u_1} = n \overline{u} \tag{33}$$

$$u = \sum_{i=1}^{k} x_i u_i \quad \text{kJ kg}^{-1} \tag{34}$$

$$\overline{u} = \sum_{i=1}^{k} y_i \overline{u_i} \quad \text{kJ kmol}^{-1} \tag{35}$$

Enthalpy

$$H = H_1 + H_2 + \cdots + H_k = \sum_{i=1}^{k} H_i \tag{36}$$

$$H = m_1 h_1 + m_2 h_2 + \cdots + m_k h_k = \sum_{i=1}^{k} m_i h_i = mh \tag{37}$$

$$H = n_1 \overline{h_1} + n_2 \overline{h_2} + \cdots + n_k \overline{h_k} = \sum_{i=1}^{k} n_i \overline{h_1} = n\overline{h} \tag{38}$$

$$h = \sum_{i=1}^{k} x_i h_i \quad \text{kJ kg}^{-1} \tag{39}$$

$$\overline{h} = \sum_{i=1}^{k} y_i \overline{h_i} \quad \text{kJ kmol}^{-1} \tag{40}$$

Entropy

$$S = S_1 + S_2 + \cdots + S_k = \sum_{i=1}^{k} S_i \tag{41}$$

$$S = m_1 s_1 + m_2 s_2 + \cdots + m_k s_k = \sum_{i=1}^{k} m_i s_i = ms \tag{42}$$

$$S = n_1 \overline{s_1} + n_2 \overline{s_2} + \cdots + n_k \overline{s_k} = \sum_{i=1}^{k} n_i \overline{s_1} = n\overline{s} \tag{43}$$

$$s = \sum_{i=1}^{k} x_i s_i \quad \text{kJ kg}^{-1} \tag{44}$$

$$\overline{s} = \sum_{i=1}^{k} y_i \overline{s_i} \quad \text{kJ kmol}^{-1} \tag{45}$$

For all extensive (depending on system size) properties:

$$A = ma = n\overline{a} = \sum_{i=1}^{k} A_i = \sum_{i=1}^{k} m_i a_i = \sum_{i=1}^{k} n_1 \overline{a_i} \tag{46}$$

For all specific (u, h, s, V, ϕ, ψ) properties:

$$a = \sum_{i=1}^{k} x_i a_i \tag{47}$$

$$\overline{a} = \sum_{i=1}^{k} y_i \overline{a_i} \tag{48}$$

0.6.1 Change in Properties

Given:

$$U = \sum_{i=1}^{k} m_i u_i \tag{49}$$

Differentiation:

$$dU = d\left(\sum_{i=1}^{k} m_i u_i\right) = \sum_{i=1}^{k} d\left(m_i u_i\right) \tag{50}$$

$$dU = \sum_{i=1}^{k} m_i \, du_i + \sum_{i=1}^{k} u_i \, dm_i \tag{51}$$

Change in mixture properties are due to 2 parts:

- changing component property $\longrightarrow du_i$
- changing composition $\longrightarrow dm_i$

For non-reacting mixture, fixed composition $\longrightarrow dm_i = 0$. Hence:

$$dU = \sum_{i=1}^{k} m_i \, du_i \tag{52}$$

$$du = \sum_{i=1}^{k} x_i \, du_i \tag{53}$$

In general:

$$dA = \sum_{i=1}^{k} m_i \, da_i \tag{54}$$

$$da = \sum_{i=1}^{k} x_i \, da_i \tag{55}$$

0.6.2 Specific Heats of Ideal Gas Mixture

Evaluating C_v and C_p of the mixture (volumetric analysis)

Given:

$$\overline{u} = \sum_{i=1}^{k} y_i \overline{u_i} \quad \text{and} \quad \overline{h} = \sum_{i=1}^{k} y_i \overline{h_i} \tag{56}$$

Differentiation with respect to temperature leads to:

$$\overline{c_v} = \sum_{i=1}^{k} y_i \overline{c}_{v,i} \quad \text{and} \quad \overline{c_p} = \sum_{i=1}^{k} y_i \overline{c}_{p,i} \tag{57}$$

The specific ratio of heats of the mixture:

$$\gamma = \frac{\overline{c_p}}{\overline{c_v}} \tag{58}$$

Evaluating C_v and C_p of the mixture (gravimetric analysis)

Define specific heats for single component i as:

$$\mathrm{d}u_i = c_{v,i}\,\mathrm{d}T_i \qquad \text{and} \qquad \mathrm{d}h_i = c_{p,i}\,\mathrm{d}T_i \tag{59}$$

For equilibrium conditions:

$$\mathrm{d}T_i = \mathrm{d}T \tag{60}$$

$$\mathrm{d}u = \sum_{i=1}^{k} x_i c_{v,i}\,\mathrm{d}T \qquad \text{and} \qquad \mathrm{d}h = \sum_{i=1}^{k} x_i c_{p,i}\,\mathrm{d}T \tag{61}$$

Also:

$$\mathrm{d}u = c_v\,\mathrm{d}T \qquad \text{and} \qquad \mathrm{d}h = c_p\,\mathrm{d}T \tag{62}$$

Therefore:

$$c_v = \sum_{i=1}^{k} x_i c_{v,i} \qquad \text{and} \qquad c_p = \sum_{i=1}^{k} x_i c_{p,i} \tag{63}$$
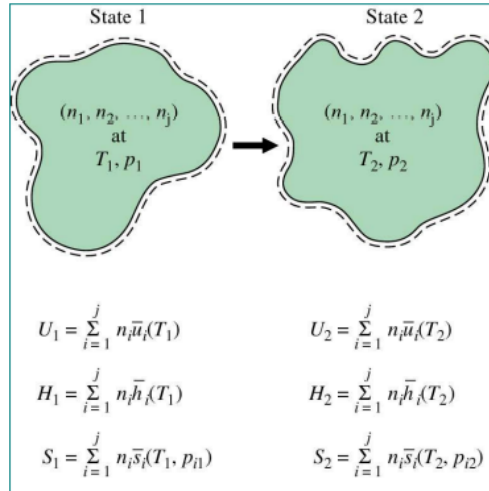
0.6.3 Change in Properties of Mixture (non-reacting)

Figure 6:

$$U_2 - U_1 = \sum_{i=1}^{j} n_i \left[\overline{u}_i(T_2) - \overline{u}_i(T_1) \right] \tag{64}$$

$$\Delta \overline{u} = \sum_{i=1}^{j} y_i \left[\overline{u}_i(T_2) - \overline{u}_i(T_1) \right] \tag{65}$$

$$H_2 - H_1 = \sum_{i=1}^{j} n_i \left[\overline{h}_i(T_2) - \overline{h}_i(T_1) \right] \tag{66}$$

$$\Delta \bar{h} = \sum_{i=1}^{j} y_i \left[\bar{h}_i(T_2) - \bar{h}_i(T_1) \right] \tag{67}$$

$$S_2 - S_1 = \sum_{i=1}^{j} n_i \left[\bar{s}_i(T_2, p_{i2}) - \bar{s}_i(T_1, p_{i1}) \right] \tag{68}$$

$$\Delta \bar{s} = \sum_{i=1}^{j} y_i \left[\bar{s}_i(T_2, p_{i2}) - \bar{s}_i(T_1, p_{i1}) \right] \tag{69}$$

Changes in mixture properties are written in terms of the respective property changes of the components, weighted by the mole fraction.

Changes in properties for component i can be evaluated by:

- Either integration of the relevant equations or
- Tabulation of ideal gas properties

0.6.4 Change in Entropy of Ideal Gas Mixtures

At fixed composition:

$$\mathrm{d}s = \sum_{i=1}^{k} x_i \, \mathrm{d}s_i \tag{70}$$

For an ideal gas mixture:

$$\mathrm{d}s = c_p \frac{\mathrm{d}T}{T} - R \frac{\mathrm{d}p}{p} \tag{71}$$

$$\Delta s = \int_{T_1}^{T_2} c_p \frac{\mathrm{d}T}{T} - R \ln \left(\frac{p_2}{p_1} \right) \tag{72}$$

$$\Delta s = s_2^\circ - s_1^\circ - R \ln \left(\frac{p_2}{p_1} \right) \tag{73}$$

Where:

$$c_p = \sum_{i=1}^{k} x_i c_{p,i} \quad \text{and} \quad R = \frac{R_u}{M} \tag{74}$$

For constant specific heat:

$$\Delta s = c_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{p_2}{p_1} \right) \tag{75}$$

Then:

$$\Delta s = \sum_{i=1}^{k} x_i \Delta s_i^\circ - \sum_{i=1}^{k} x_i R_i \ln \left(\frac{p_{i,2}}{p_{i,1}} \right) \tag{76}$$

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For constant specific heat:

$$\Delta s = \sum_{i=1}^{k} x_i c_{p,i} \ln \left(\frac{T_2}{T_1} \right) - \sum_{i=1}^{k} x_i R_i \ln \left(\frac{p_{i,2}}{p_{i,1}} \right) \tag{77}$$

On a molar basis:

$$\Delta \bar{s} = \sum_{i=1}^{k} y_i \Delta \bar{s}_i^{\circ} - \sum_{i=1}^{k} y_i R_u \ln \left(\frac{p_{i,2}}{p_{i,1}} \right) \tag{78}$$