

MME 2009

Metallurgical

Thermodynamics

Course 2 - Mathematical Tools and Unit
Conversion Used in Thermodynamic Problem
Solving

Basic Algebra Computations

1st degree equations - $ax + b = 0$

Collect numerical values on one side and unknown to the otherside to find the root

2nd degree equations - $ax^2 + bx + c = 0$

Use discriminant equations

$$x_{1,2} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Complex equations containing higher degree logarithmic, exponential terms

$$a + bx + cx^2 + dx^3 + e \log x = 0$$

Use graphical method

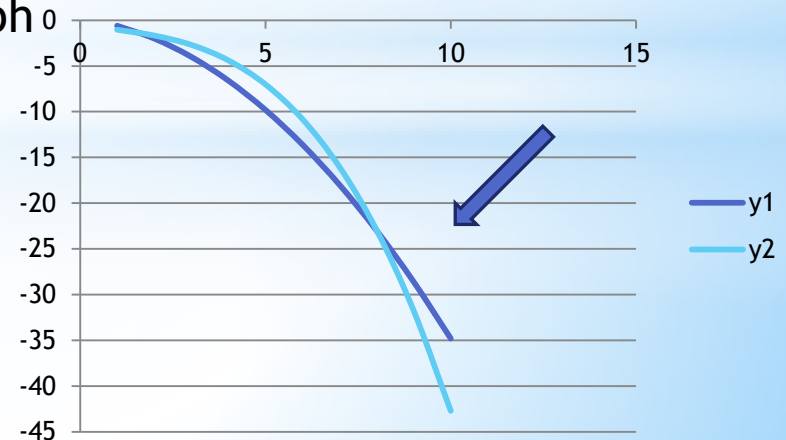
I. Seperate the equation into two parts

$$\underbrace{a + bx + cx^2}_{y_1} = \underbrace{-dx^3 - e \log x}_{y_2}$$

II. Prepare a table of y_1 versus y_2 with values of x within the domain

III. Plot both y_1 and y_2 versus x on the same graph

| x | y1 | y2 |
|----|-------|----------|
| 1 | -0.6 | -1.04 |
| 2 | -2 | -1.67125 |
| 3 | -4 | -2.69143 |
| 4 | -6.6 | -4.38588 |
| 5 | -9.8 | -7.01168 |
| 6 | -13.6 | -10.8174 |
| 7 | -18 | -16.0482 |
| 8 | -23 | -22.9472 |
| 9 | -28.6 | -31.7567 |
| 10 | -34.8 | -43.7193 |



Numerical method for complex equations

Successive iteration steps:

- Separate the equation into two in such a way to have one side of the equation with terms that are easy to solve

$$\underbrace{a + bx}_{y_1} = -cx^2 - dx^3 - e \log x$$

- Start the iteration by supplying an initial value for x
- Replace the numerical value of x into y_2 and obtain a numerical value for y_2

$$\underbrace{a + bx}_{y_1} = \text{constant}$$

- Solve y_1 for x
- Compare the new x with the previous x
 - If the two values are different go to the second step using the new x value
 - Repeat the process until the two successive x values are equal

Example - Calculate the mole fraction of a gas, in a binary mixture from the equation:

$$0.43x^3 - 1.28x^2 + 2.78x - 0.93 = 0$$

$$\underbrace{2.78x - 0.93}_{y_1} = \underbrace{1.28x^2 - 0.43x^3}_{y_2}$$

| x | y2 | y1 | x |
|--------|----------|----------|--------|
| 0.1 | 0.01323 | 0.01323 | 0.3378 |
| 0.3378 | 0.162634 | 0.162634 | 0.38 |
| 0.38 | 0.208427 | 0.208427 | 0.41 |
| 0.41 | 0.2248 | 0.2248 | 0.423 |
| 0.423 | 0.2315 | 0.2315 | 0.429 |
| 0.429 | 0.2322 | 0.2322 | 0.43 |

Thermodynamics is a science dealing with energy changes, state changes and property changes

$$\Delta E = \Delta E_K + \Delta E_P + \Delta U$$

$$\Delta H = H_2 - H_1$$

$$\Delta T = \frac{\Delta PV}{R}$$

Engineering requires accurate calculations, taking into account even the infinitely small changes

$$\Delta E = \int dE_K + \int dE_P + \int dU$$

$$\Delta H = \int_{H_1}^{H_2} dH$$

$$\Delta T = \int dT = \frac{P}{R} \int dV$$

Differential equations and their integrals enable engineers make detailed analysis of problems involving changes big or small

Continuous paths of reversible processes also necessitate the use of differential equations

Total differential equations

$$z = f(x, y)$$

$$dz = \left(\frac{dz}{dx}\right)_y dx + \left(\frac{dz}{dy}\right)_x dy$$

Useful relationships can be developed from total differential equation by taking z constant

$$0 = \left(\frac{dz}{dx}\right)_y (dx)_z + \left(\frac{dz}{dy}\right)_x (dy)_z$$

dividing by dy

$$0 = \left(\frac{dz}{dx}\right)_y \left(\frac{dx}{dy}\right)_z + \left(\frac{dz}{dy}\right)_x$$
$$-\left(\frac{dz}{dy}\right)_x = \left(\frac{dz}{dx}\right)_y \left(\frac{dx}{dy}\right)_z$$

dividing by $\left(\frac{dz}{dy}\right)_x$

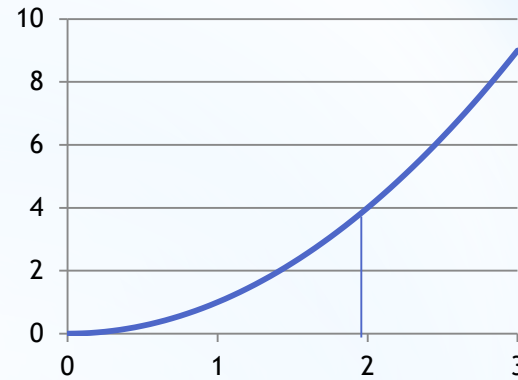
$$-1 = \left(\frac{dz}{dx}\right)_y \left(\frac{dx}{dy}\right)_z \left(\frac{dy}{dz}\right)_x$$

Transformation formula

Line integrals

Integrating a simple function such as $y = x^2$ between the limits gives the area under the curve

$$y = \int_0^2 x^2 = \frac{2^3}{3} = \frac{8}{3}$$



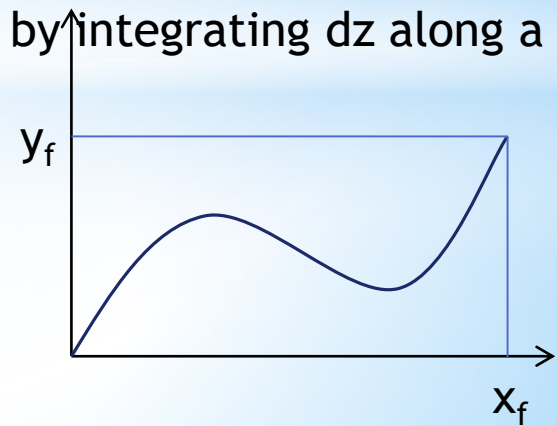
Thermodynamic functions often contain more than one independent variable

$$dz = M(x, y)dx + N(x, y)dy$$

Solutions to thermodynamic problems are often done using paths or curves

Total change in z can be obtained between the limits by integrating dz along a given curve

$$\int_{z_i}^{z_f} dz = \oint_{x_i, y_i}^{x_f, y_f} M(x, y)dx + N(x, y)dy$$



Steps:

- I. Calculate variables and the derivatives in terms of each other using curve equation
 - Main function: $dz = 2x^3y^2dx + y/x dy$ Path: $y = 1/x$
- II. Replace them in the integral in such a way to have only one variable in each part of the integral
 - $dz = 2x^3 \cdot 1/x^2 dx + y^2 dy$
- III. Evaluate the integral between the limits
 - $\int_0^2 dz = x^2 + \frac{y^3}{3} = 4 + \frac{8}{3}$

Example - Calculate the change in z between (0,0) and (1,1) for $dz = x^2ydx + xy^2dy$ along the following paths

a) $y=x$

b) $y=x^2$

c) $(0,0) \rightarrow (1,0) \rightarrow (1,1)$

Exact differentials

The value of Δz becomes independent of the path when certain conditions are met. This situation is encountered when dz is an exact differential

$$dz = M(x, y)dx + N(x, y)dy$$

For a differential to be exact, it has to meet the Euler's criteria:

$$\left(\frac{\partial M(x, y)}{\partial y}\right)_x = \left(\frac{\partial N(x, y)}{\partial x}\right)_y$$

Example - Calculate the change in z between $(0,0)$ and $(1,1)$ for the function $dz = (2x + y)dx + (x + 2y)dy$ along the following paths:

a) $y=x$

b) $y=x^2$

c) $(0,0) \rightarrow (1,0) \rightarrow (1,1) \rightarrow (0,1) \rightarrow (0,0)$

Question - Which one of the following statements correctly describes the term *state property*?

- a) A state property gives a complete description of the system
- b) A state property describes any system property that is conserved
- c) A state property indicates which microstate the system is in
- d) A state property is a property that does not depend on the history of the system
- e) A state property describes the amount of heat added to or removed from a system

Units and conversion factors

Mass - absolute quantity of matter

m - mass, kg

Velocity - distance per unit time

$$v = \frac{d}{t} \frac{m}{\text{sec}} \quad \text{where:}$$

v - velocity in m/sec
d - distance in meters
t - time in sec

Acceleration - the rate of change of velocity with respect to time

$$a = \frac{dv}{dt} \frac{m}{\text{sec}^2}$$

Force - the mass multiplied by the acceleration

$$F = ma \frac{\text{kg} \cdot \text{m}}{\text{sec}^2} \text{ or Newton}$$

$$F = \frac{ma}{1000} \text{ KN}$$

$$1 \text{ Newton} = 1 \text{ kg} \cdot \text{m} / \text{sec}^2$$

Newton - the force required to accelerate 1 kg mass at the rate of 1 m/sec

Weight - the force due to gravity

$$W = mg \text{ N}$$

$$W = \frac{mg}{1000} \text{ KN}$$

Where:

g – gravitational acceleration, m/sec^2

At standard sea level condition

$$g = 9.81 \text{ m/sec}^2$$

Density - the mass per unit volume

$$\rho = \frac{m}{V} \frac{\text{kg}}{\text{m}^3}$$

Where;

ρ - density in kg/m^3

m – mass in kg

V – volume in m^3

Specific volume - the volume per unit mass or the reciprocal of its density

$$v = \frac{V}{m} = \frac{1}{\rho} \frac{\text{m}^3}{\text{kg}}$$

Where:

v - specific volume in m^3/kg

Specific weight - the weight per unit volume.

$$\gamma = \frac{W}{V} = \frac{mg}{1000V} = \frac{\rho g}{1000} \frac{\text{KN}}{\text{m}^3}$$

Where:

γ - specific weight in KN/m^3

$$\text{For Liquids: } S_L = \frac{\rho_L}{\rho_w}$$

Specific gravity or relative density

For liquids it is the ratio of its density to that of water at standard temperature and pressure.

$$\text{For Gases: } S_G = \frac{\rho_G}{\rho_{AH}}$$

For gases it is the ratio of its density to that of either air or hydrogen at some specified temperature and pressure

Pressure - force per unit area

$$P = \frac{F}{A} = \frac{ma}{A} = \frac{\text{kg}}{\text{sec}^2\text{m}} \text{ or Newton per meter squared or Pascal}$$

Atmospheric Pressure - the absolute pressure exerted by the atmosphere

At Standard Condition

$$\begin{aligned} 1 \text{ atm} &= 101.325 \text{ KPa} \\ &= 1.033 \text{ kg/cm}^2 \\ &= 0.101325 \text{ MPa} \\ &= 1.01325 \text{ Bar} \\ &= 760 \text{ mm Hg} \\ &= 76 \text{ cm Hg} \\ &= 14.7 \text{ lb/in}^2 \\ &= 10.33 \text{ m of H}_2\text{O} \\ &= 29.921 \text{ in of Hg} \\ &= 33.88 \text{ ft of H}_2\text{O} \end{aligned}$$

Work - force acting through a distance

$$W = Fl = mal = PV = \frac{\text{kg m}^2}{\text{sec}^2} \text{ or Newton meter or liter atm or Joule}$$

Energy - the capacity to perform work

Kinetic energy - Force applied to a body to move a distance

$$dW = madl$$

$$dW = m \frac{dv}{dt} dl = m \frac{dl}{dt} dv$$

$$dW = mvdv$$

$$W = m \int_{v_1}^{v_2} v dv = m \left(\frac{v_2^2 - v_1^2}{2} \right)$$

$$W = \frac{mv_2^2}{2} - \frac{mv_1^2}{2}$$

$$E_K = \frac{1}{2} mv^2 \quad \text{Newton meter or Joule}$$

Potential energy - Upward force exerted on a body to raise to an elevation

$$F = ma = mg$$

$$W = F(h_2 - h_1) = mg(h_2 - h_1)$$

$$E_P = mgh \quad \text{Newton meter or Joule}$$

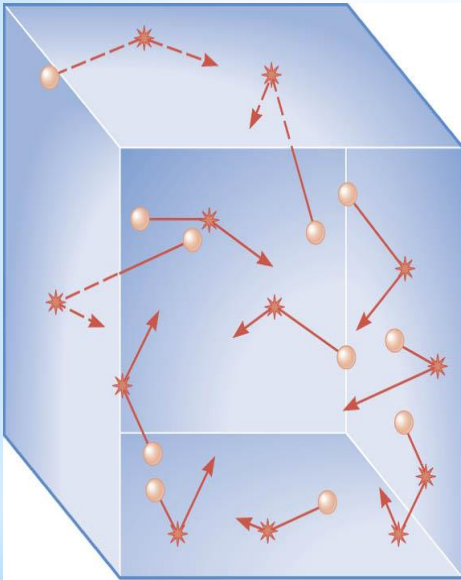
Power - Energy output rate of one Joule per second

Newton meter / second or Watt

Temperature - the degree of intensity of heat

Measured with liquid-in-glass thermometers where the liquid expands when heated

Temperature scale of the SI system is based on the ideal gas as thermometric fluid



Ideal gas is made up of particles or molecules

Each particle in a gas has kinetic energy

All collisions are perfectly elastic

Volume of the particles is insignificant

There are no interactions between particles

The average kinetic energy of the particles is a function of only absolute temperature

The volume of the gas is zero at absolute zero

$$v_{ave} = \sqrt{\frac{3RT}{M}}$$

Where;

R - gas constant =
8.3144 joules/degree mole
M - Molar mass kg/mole

The temperature relates to the average of the whole sample, as there is one temperature for the sample

Temperature Conversion

| | Kelvin | Celsius | Rankine | Fahrenheit |
|------------------------------|--------|---------|---------|------------|
| Steam/boiling point of water | 373° | 100° | 672° | 212° |
| Ice/freezing point of water | 273° | 0° | 492° | 32° |
| Solid CO ₂ | 195° | -78° | 351° | -109° |
| Liquid oxygen point | 90° | -183° | 162° | -297° |
| Absolute zero | 0° | -273° | 0° | -460° |

Absolute temperature

Table 3: Temperature Conversions

| Scale | To Kelvin | From Kelvin | Scale | To Celsius | From Celsius |
|-------------------|------------------------------------|--------------------------------------|-------------------|--|---|
| Celsius | $K = ^\circ C + 273.15$ | $^\circ C = K - 273.15$ | Fahrenheit | $^\circ C = (^\circ F - 32) \div 1.8$ | $^\circ F = (1.8 \times ^\circ C) + 32$ |
| Fahrenheit | $K = (^\circ F + 459.67) \div 1.8$ | $^\circ F = (K \times 1.8) - 459.67$ | Rankine | $^\circ C = (^\circ R + 1.8) - 273.15$ | $^\circ R = 1.8 \times (^\circ C + 273.15)$ |
| Rankine | $K = ^\circ R \div 1.8$ | $^\circ R = 1.8 \times K$ | Kelvin | $^\circ C = K - 273.15$ | $K = ^\circ C + 273.15$ |

| Scale | To Rankine | From Rankine | Scale | To Fahrenheit | From Fahrenheit |
|-------------------|---|---|----------------|---|---------------------------------------|
| Celsius | $^\circ R = 1.8 \times (^\circ C + 273.15)$ | $^\circ C = (^\circ R \div 1.8) - 273.15$ | Celsius | $^\circ F = (1.8 \times ^\circ C) + 32$ | $^\circ C = (^\circ F - 32) \div 1.8$ |
| Fahrenheit | $^\circ R = ^\circ F + 459.67$ | $^\circ F = ^\circ R - 459.67$ | Rankine | $^\circ F = ^\circ R - 459.67$ | $^\circ R = ^\circ F + 459.67$ |
| Kelvin | $^\circ R = 1.8 \times K$ | $K = ^\circ R \div 1.8$ | Kelvin | $^\circ F = (1.8 \times K) - 459.67$ | $K = (^\circ F + 459.67) \div 1.8$ |

Gas constant R

Ideal gas obeys Boyle's law, Charle's law and Avogadro's law

$$V_T \propto \frac{1}{V} \quad V_P \propto T \quad \gamma \propto M$$
$$P_V \propto T$$

Ideal Gas Equation of State:

$$\frac{PV}{T} = \text{constant}$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = R$$

$$PV = nRT$$

| Values of R | Units |
|-----------------------------|---|
| 8.3144621 | J · K ⁻¹ · mol ⁻¹ |
| 0.082057 | L · atm · K ⁻¹ · mol ⁻¹ |
| 8.205736 × 10 ⁻⁵ | m ³ · atm · K ⁻¹ · mol ⁻¹ |
| 8.3144621 | L · kPa · K ⁻¹ · mol ⁻¹ |
| 8.3144621 | m ³ · Pa · K ⁻¹ · mol ⁻¹ |
| 62.36368 | L · mmHg · K ⁻¹ · mol ⁻¹ |
| 62.36359 | L · torr · K ⁻¹ · mol ⁻¹ |
| 83.144621 | L · mbar · K ⁻¹ · mol ⁻¹ |
| 10.73158 | ft ³ · psi · °R ⁻¹ · lb-mol ⁻¹ |
| 0.73024 | ft ³ · atm · °R ⁻¹ · lb-mol ⁻¹ |

The *R* value given by the National Institute of Standards and Technology (NIST) is 8.314462 J · K⁻¹ · mol⁻¹ as of 2010.

Volume per gram-mole of ideal gas at 0 °C and 1 atm is 22.414 liters according to Avogadro's law

Thus

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \frac{1 \text{ atm} * 22.414 \text{ liters}}{273.15 \text{ degree} * \text{mole}} = 0.082057 \text{ liter} * \text{atm} / \text{degree} * \text{mole}$$

Heat - the form of energy transferred from hot to cold objects

It is energy in transit, not stored in the system as heat but as kinetic and potential energy of the atoms

The rate of heat transfer from one body to another is proportional to the difference in temperature

1 calorie = the quantity of heat required to raise the temperature of 1 gram of water by 1 °C = 4.1840 Joules

Specific Heat

Specific Heat or Heat Capacity is the amount of heat required to raise the temperature of a 1 kg mass by 1°C

$$Q = mC\Delta T$$

Example - What quantity of heat is required to change the temperature of 200 g of lead from 20 to 100°C?

$$C_{\text{Pb}} = 130 \text{ J/kg.K}$$

Example - An oven applies 400 kJ of heat to a 4 kg of a substance causing its temperature to increase by 80 C°. What is the specific heat capacity?

Example - How many grams of iron at 20°C must be heated to 100°C in order to be able to release 1800 cal of heat as it returns to its original temperature?

$$C_{\text{Pb}} = 113 \text{ cal/kg.K}$$

| Quantity | Conversion | Quantity | Conversion |
|----------|--|----------|---|
| Length | $1 \text{ m} = 100 \text{ cm}$ $= 3.28084(\text{ft}) = 39.3701(\text{in})$ | Volume | $1 \text{ m}^3 = 10^6 \text{ cm}^3 = 10^3 \text{ liters}$ $= 35.3147(\text{ft})^3$ $= 264.172(\text{gal})$ |
| Mass | $1 \text{ kg} = 10^3 \text{ g}$ $= 2.20462(\text{lb}_m)$ | Density | $1 \text{ g cm}^{-3} = 10^3 \text{ kg m}^{-3}$ $= 62.4278(\text{lb}_m)(\text{ft})^{-3}$ |
| Force | $1 \text{ N} = 1 \text{ kg m s}^{-2}$ $= 10^5(\text{dyne})$ $= 0.224809(\text{lb}_f)$ | Energy | $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2} = 1 \text{ N m}$ $= 1 \text{ m}^3 \text{ Pa} = 10^{-5} \text{ m}^3 \text{ bar} = 10 \text{ cm}^3 \text{ bar}$ $= 9.86923 \text{ cm}^3(\text{atm})$ $= 10^7(\text{dyne}) \text{ cm} = 10^7(\text{erg})$ $= 0.239006(\text{cal})$ $= 5.12197 \times 10^{-3}(\text{ft})^3(\text{psia}) = 0.737562(\text{ft})(\text{lb}_f)$ $= 9.47831 \times 10^{-4}(\text{Btu}) = 2.77778 \times 10^{-7} \text{ kWhr}$ |
| Pressure | $1 \text{ bar} = 10^5 \text{ kg m}^{-1} \text{ s}^{-2} = 10^5 \text{ N m}^{-2}$ $= 10^5 \text{ Pa} = 10^2 \text{ kPa}$ $= 10^6(\text{dyne}) \text{ cm}^{-2}$ $= 0.986923(\text{atm})$ $= 14.5038(\text{psia})$ $= 750.061(\text{torr})$ | Power | $1 \text{ kW} = 10^3 \text{ W} = 10^3 \text{ kg m}^2 \text{ s}^{-3} = 10^3 \text{ J s}^{-1}$ $= 239.006(\text{cal}) \text{ s}^{-1}$ $= 737.562(\text{ft})(\text{lb}_f) \text{ s}^{-1}$ $= 0.947831(\text{Btu}) \text{ s}^{-1}$ $= 1.34102(\text{hp})$ |