Chapter 1: Introduction

CHEMICAL ENGINEERING THERMODYNAMICS

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Objectives for Chapter 1

- Dimensions and Units
- Understanding basic concepts
- Language of Thermodynamics
- Concepts of Temperature & Pressure
- Difference between Heat and Work
- Energy and Energy Conservation

Dimensions and Units

- Essential when measuring quantities
- Dimensions are recognized by sensory perceptions, their use requires a scale of measurement, known as unit.
- Every quantity measured has a standard unit associated with it
- Dimensions / Units are classified a
  - **Fundamental** e.g. length (m), time (s)
  - **Derived** e.g. force (N), density (kg/m^3)

System of Units

- There are basically two systems of units English (fps) and metric (cgs, mks) system.
- To obtain international agreement on questions of metrology, the Système International d’ Unités (abbreviated SI units) was agreed on at the Eleventh General Conference on Weights and Measures.
- Generally SI units are used in engineering, with lapses to use of common units such as volume in liters and pressure in bar.
- Use scaling prefixes, with either large numbers or smaller numbers.

Prefixes for SI Units

Multiplication Factor	Prefix	Symbol
10^{12}	tera	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	k (e.g. kilogram)
10^{-2}	centi	c (e.g. centimeter)
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9} `	nano	n
10^{-12}	pico	p
10^{-15}	femto	f

Illustration

The density of mercury is 13.5 g cm^{-3}. I push 10 ml of mercury 200 mm along the bench with a force which accelerates the blob at 5 m s^{-2}, how much energy have I expended?

<u>Step 1</u> Note what is asked (in this case energy)

<u>Step 2</u> Note what is given (density, volume, distance and acceleration)

<u>Step 3</u> Convert everything to SI units

<u>Step 4</u> Choose equations and solve problem

Units

<u>Step 3</u> Convert everything to SI base

13.5 g cm^{-3} is 13.5 x10^{-3} kg cm^{-3} is 1.35 x 10^{-2} kg cm^{-3} is 1.35 x 10^{4} kg m^{-3}

10 ml is 10 cm^{3} is 10 x 10^{-6} m^{3} is 1 x 10^{-5} m^{3}

200 mm is 0.2 m

<u>Step 4</u> Choose the correct equation/ equations

We know that Energy is Force x distance; Force is mass x acceleration; Density is mass/volume

Units

Mass is density x volume = $1.35 \times 10^4 \times 1 \times 10^{-5}$ = 0.135 kg (kg m^{-3} x m^3)
Force is mass x acceleration = 0.135 x 5 = 0.675 N (kg m s^{-2} = kg x m s^{-2})
Energy is Force x distance = 0.675 x 0.2 = 0.135 J (kg m^2 s^{-2} = kg m s^{-2} x m)

When you use equations, you must always be aware of the units. The equation is only true if SI units are used

Measure of Amount or Size

Three measures of amount or size

Mass (m) Number of moles (n) Total volume (V^t)

Mass Quantity of matter in a substance

Number of moles Mass divided by molar mass (or molecular weight)

Total Volume Represent the size of the system and given as the products of the three length

- **Specific volume:** $V = V^t/m$
- **Molar volume:** $v = V^t/n$

* Specific or molar density are reciprocal of specific and molar volume respectively

Force

Derived from Newton's second law of motion

***F = ma* (SI unit newton)**

<u>Weight</u> Gravitational FORCE acting on a substance

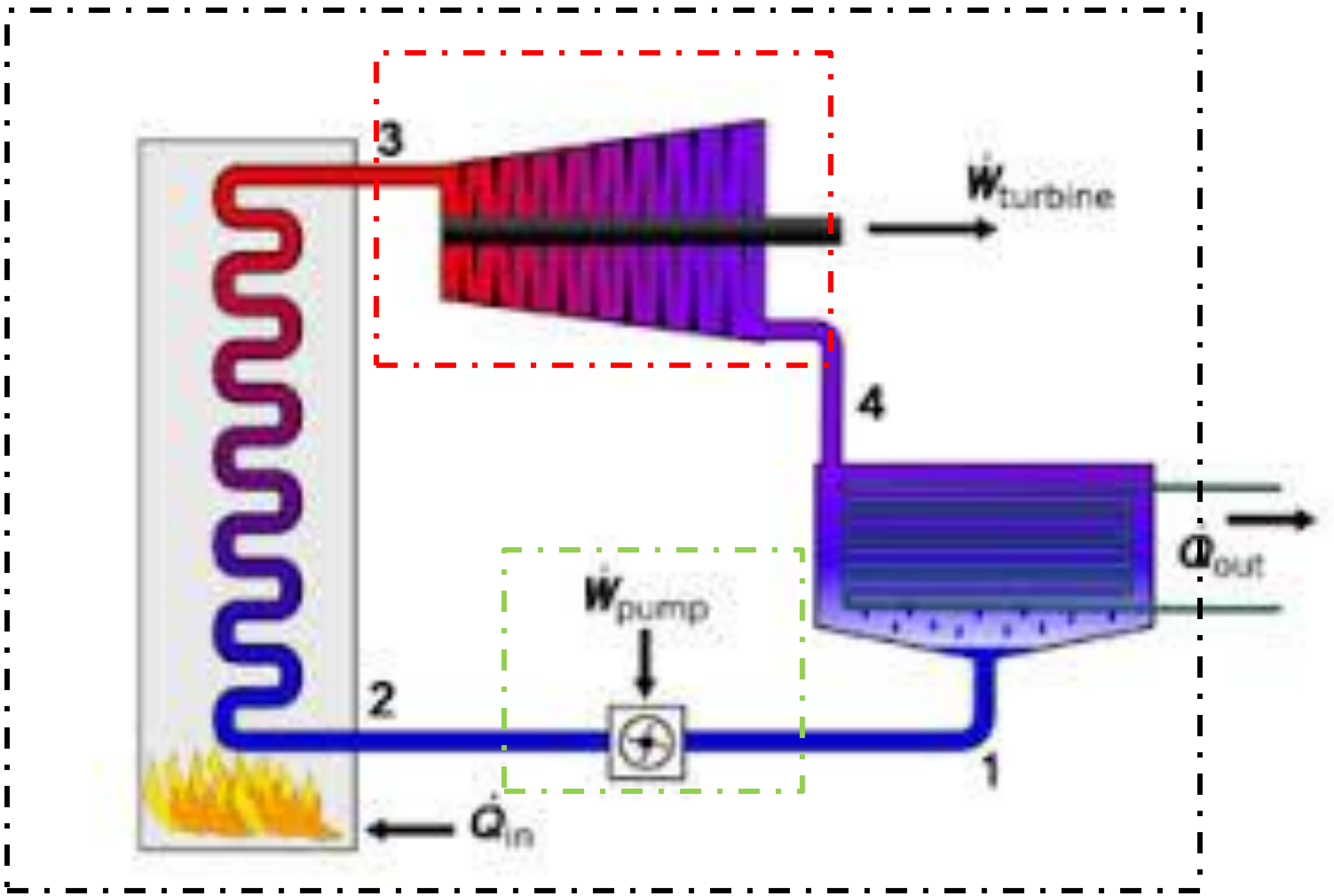
Weight (A FORCE) = mass (kg) x gravitational acceleration (m / s²)

The newton is defined as the force when applied to a mass of 1 kg produces an acceleration of 1 m/s^2.

The kilogram force is so defined that a standard gravitational field exerts a force of 1 kg on a mass of 1 kg.

$$1\,\text{kgf} = \frac{1}{g_c}\,\text{X}\,1\,\text{kg}\,\text{X}\,9.80665\,\text{m/s}^2 \quad \text{or} \quad g_c = 9.80665\,\text{kg m kgf}^{-1}\,\text{s}^{-2}$$

Language of Thermodynamics



The Language of Thermodynamics

- **SYSTEM**

  Small part of the universe, e.g., within a steam engine, a laboratory beaker, or a chemical reactor focused for study

  This may be a specified volume (control volume) or quantity of matter (fixed mass) in space

- **SURROUNDINGS**

  Everything external to the system (** More realistically, the surrounding may be visualized as only that part of universe which is affected by process occurring within system)

System separated from surroundings by a system boundary

The Language of Thermodynamics

<u>System –surrounding Interaction</u>

- A system is said to be in contact with its surroundings if a change in surroundings can produce in change in the system or vice versa
  - If mass can flow into or out of the system, it is said to be **open system**
  - If no, the system is ***closed system***

- If a system does not change as a result of changes in the surroundings, the system is said to be ***isolated***

The Language of Thermodynamics

To define the system completely some physically measurable quantities (or characteristics) must be specified, which are called ***system's properties*** (temperature, pressure, volume)

Independent Properties

Minimum number of properties required to define the ***state*** of a system (If a state of a system is known, all its properties are fixed)

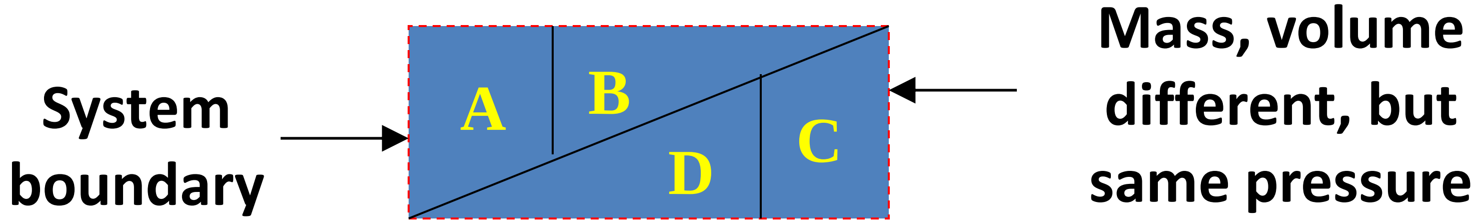
Dependent Properties

Properties determined in terms of values of independent properties

The Language of Thermodynamics

Extensive properties These are properties that depend on the extent of the system. E.g: length, volume, mass etc.

Intensive properties These are properties that do no depend on the extent of the system. E.g: pressure, temperature, density



Ratio of two extensive properties of a homogeneous system is an intensive property

For e.g. mass per unit volume is density which is intensive

The Language of Thermodynamics

Equilibrium State

- A system is said to be in thermodynamic equilibrium if there is no finite spontaneous change in the state of the system
- All intensive properties are same and there is no scope for change
- All influences which cause change/ disturbance (driving forces) are counterbalanced
  - For a stable equilibrium stable state, with respect to disturbances the properties of state do not depend on the path followed to approach the equilibrium

The Language of Thermodynamics

Thermodynamic Process

- A ***process*** is said to be occur in a system when any sort of change or transformation, chemical or physical, takes place.
- During a process, the system changes from an *initial state* through a series of intermediate states to a *final state*. This series of states is called the ***path*** of process.
- A ***cyclic process*** is said to be occurred within a system when, after changing from some initial state to some second state, it's restored to its initial state (but the surroundings may not have undergone a cyclic process)

The concept of temperature

While rigorous definition arises from the 2nd Law of thermodynamics, the basic concept arises from sensory perception of hotness and coldness.

Equality of temperature

Two blocks in thermal contact with each other, but isolated from its environment will attain temperature equality over a period of time and observable properties after thermalequilibrium will no longer change.

- **Temperature is a thus a property which can govern *thermal equilibrium* between systems**

The concept of temperature

- The Zeroth law provides the basis for measurement of <u>temperature</u>

It allows us to compare temperatures of two bodies A and B with the help of a third body C and say A and B are at the same temperature without bringing them in contact (principle of the thermometer)

Properties of substance used to measure temperature are referred to as **thermometric properties** e.g volume, resistance, emf etc. These properties are a function of temperature

The concept of temperature

Temperature scales Required to assign quantitative values to temperature

- Mostly established empirically by using a relationship between temperature and a thermometric property
- Two common scales developed: Celsius and Fahrenheit scale
  - For the Celsius scale ice point is 0, and the boiling point of water is 100
- Later **absolute scales**: Kelvin and Rankine scales were developed
  - In thermodynamics, absolute temperature is implied by an unqualified reference to temperature

Temperature Scales

The relation between the Fahrenheit and Celsius scales

$$t\,(^{o}C\,)/\,100 = [t\,(^{o}F) - 32]\,/\,180$$

$$T\,(K) = T\,(^{o}C) + 273.15$$

$$T\,(R) = t\,(^{o}F) + 459.67$$

$$T\,(R) = 1.8\,T\,K$$

- The Celsius degree and the kelvin represents the same temperature *interval*, as do the Fahrenheit and the rankine.
- Lower limit of temperature, called absolute zero on the Kelvin scale, occurs at - 273.15 ^{o}C
- The ice point is 32 (^{o}F) rmal boiling and the normal boiling point of water is 212 (^{o}F).

Comparison between Thermometers, Calibrated Linearly form 0 to 100 ^oC and the perfect Gas Scale

Perfect Gas Scale (^oC)	Expansion of helium gas at constant pressure(^oC)	Expansion of mercury in Jena Glass 59(^oC)	e.m.f. of Chromel-Alumel Thermocouple (^oC)
400	399.95	412.6	400
300	299.98	304.4	297.8
200	199.994	200.8	198.3
50	50.001	50.03	49.3
0	0	0	0
-50	-50.002		-45.4

- The following table lists the volumes of 1 gram of water and 1 gram of water and 1 gram of mercury as functions of temperature.
    1) Discuss why water would not be an appropriate thermometer fluid between 0˚C and 10˚C.
    2) Because of the slightly nonlinear temperature dependence of the specific volume of liquid mercury, there is an inherent error in using a mercury-filled thermometer that has been calibrated against an ideal gas thermometer at only 0˚C and 100˚C. Using the data in the table, prepare a graph of the error, ΔT, as a function of temperature.
    3) Why does a common mercury thermometer consists of a large-volume mercury-filled bulb attached to a capillary tube?

T(˚C)	Vol of 1 gram of H_2O (cm^3)	Vol of 1 gram of Hg (cm^3)
0	1.0001329	0.0735560
1	1.0000733	0.0735694
2	1.0000321	0.0735928
3	1.0000078	0.0735861
4	1.0000000	0.0736095
5	1.0000081	0.0736228
6	1.0000318	0.0736362
7	1.0000704	0.0736496
8	1.0001236	0.0736629
9	1.0001909	0.0736763
10	1.0002719	0.0736893
20	1.0015678	0.0738233
30	1.0043408	0.0739572
40	1.0078108	0.0740910
50	1.012074	0.0742250
60	1.017046	0.0743592
70	1.022694	0.0744936
80	1.028987	0.0746282
90	1.035904	0.0747631
100	1.043427	0.0748981

Understanding basic properties

Pressure

- Defined as normal force per unit area
  - SI unit is Pa (Pascal) ~ 1 N/m^2
  - Pa is a small unit. Hence kPa (10^3 Pa) and MPa (10^6 Pa) used
  - Another common unit of pressure is bar (1 bar = 10^5 Pa or 100 kPa or 0.1 MPa)
- Pressure or equivalently force : related to concept of ***'mechanical equilibrium'***

Understanding basic properties

- Hydrostatic pressure: Pressure exerted by a column of fluid of height z

$$P = h\ (m) \times \rho (kg/m^3) \times g (m/s^2)$$

Pressure is also expressed as the equivalent height of a fluid column (Basis for using manometers for pressure measurement)

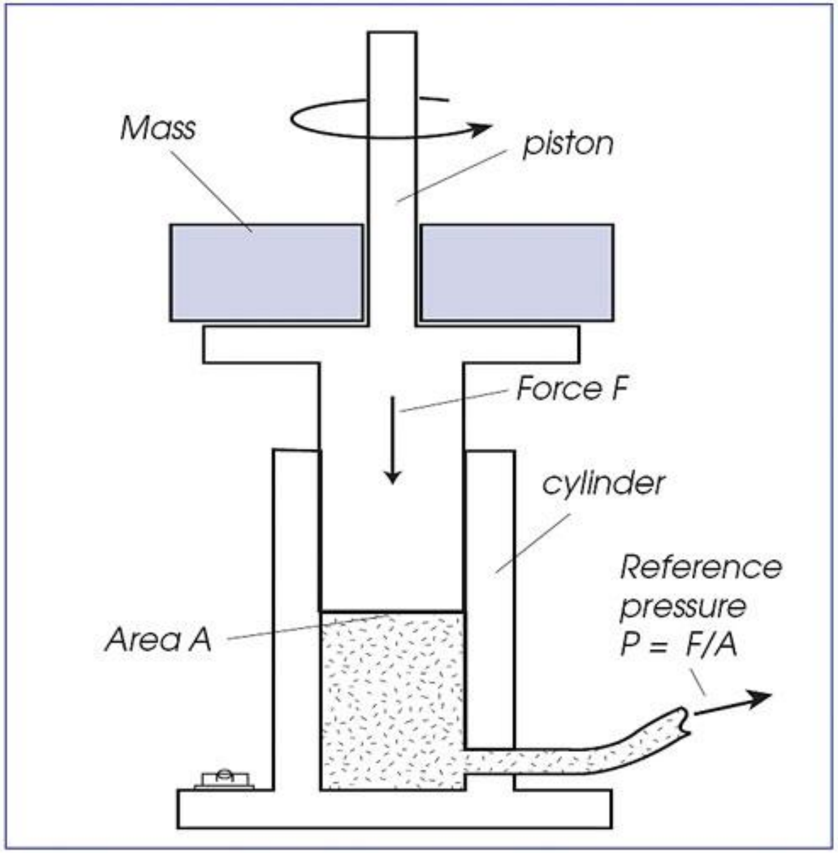
- Standard atmospheric pressure

The standard atmospheric pressure of 1 atm is defined as the approximate average pressure exerted by the earth's atmosphere at mean sea level

Note: Standard means no change universally

1 atm = 760 mm Hg = 29.92 in Hg = 101325 Pa = 1.01325 bar

Dead Weight Gauge



TH2: Schematic diagram of dead-weight pressure calibrator

- Used to measure pressure
- Known pressure are created by placing known weights on a frictionless piston
- Pressure gauges give the readings which are the difference between the pressure of interest and the pressure of the surrounding atmosphere

Absolute, Gauge and Vacuum Pressure

Pressure measured can be above or below atmospheric (vacuum)

Above atmospheric

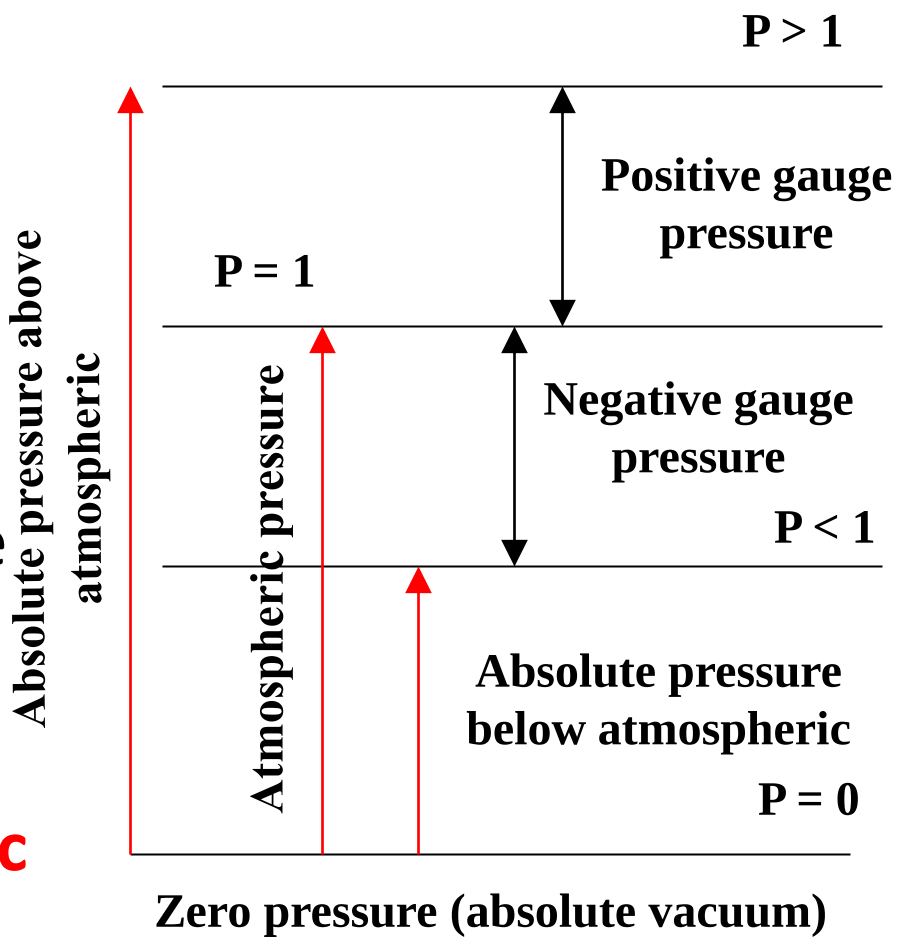
P(abs) = P (g) + P (atm)

Below atmospheric

P(abs) = P (atm) - P (g)

Either use the term negative pressure or vacuum. Do not use negative vacuum

*** Absolute pressures must be used in thermodynamic calculations**



Work

- Work is accomplished by a force acting through a distance

$$W = \int F dL$$

- Energy in *transit* across a system's boundary
- Thermodynamic Work accompanied a change in volume

$$W = -\int_{V_1^t}^{V_2^t} P . dV^t$$

  - SI unit of work is newton-meter or joule (J)
  - Work done by a system on surroundings is positive whereas work done on the system by the surroundings is negative

Energy

- Energy is an attribute of a system that takes several forms.
- Energy transferred from one system to another may be called work, heat, radiation or a variety of other names, depending on the mode or form of transfer
- There are two basic kinds of energy: kinetic energy (KE) and potential energy (PE)
- Kinetic energy is associated with motion

$$E_K \equiv \frac{1}{2} m u^2$$

- Potential energy is associated with interactions between objects

$$E_P \equiv mzg$$

- <u>Kinetic and potential energy reside with the system and their values are measured with respect to surroundings</u>.

Heat

- Heat was recognized as a form of energy, lately.
- Concept of Heat as ‘energy in transit’ gained acceptance after 1850, largely on account of the classic experiments of J.P. Joule.
- When a hot body and a cold body are in contact, the hot body loses energy and the cold body gains energy. Most physicists refer to the energy transferred in that way as “heat” (Q).
- Previuosly used units for heat were Btu (*British thermal unit*) and cal (calorie) which later defined in relation to SI unit ‘Joule’

1 cal = 4.184 J ; 1 Btu = 1054.35 J