

Thermodynamic

The science that deals with heat and work and those properties of matter that relate to heat and work, or (Energy differences and transfers between systems).

→ Describes macroscopic properties of equilibrium systems

→ Entirely Empirical

→ Built on 4 Laws and "simple" mathematics

0th Law \Rightarrow Defines Temperature (T)

1st Law \Rightarrow Defines Energy (U)

2nd Law \Rightarrow Defines Entropy (S)

3rd Law \Rightarrow Gives Numerical Value to Entropy

Definitions:

- *System*: The part of the Universe that we choose to study
- *Surroundings*: The rest of the Universe
- *Boundary*: The surface dividing the System from the Surroundings

Systems can be:

- *Open*: Mass and Energy can transfer between the System and the Surroundings
- *Closed*: Energy can transfer between the System and the Surroundings, but NOT mass
- *Isolated*: Neither Mass nor Energy can transfer between the System and the Surroundings

Describing systems requires:

- A few macroscopic properties: p, T, V, n, m, \dots
- Knowledge if System is Homogeneous or Heterogeneous
- Knowledge if System is in Equilibrium State
- Knowledge of the number of components

Two classes of Properties:

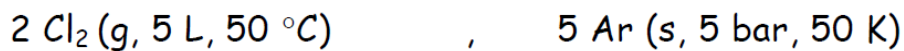
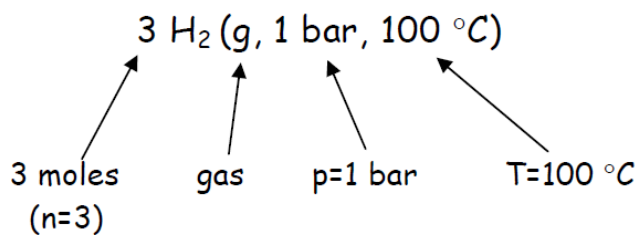
- *Extensive*: Depend on the size of the system
(n, m, V, \dots)
- *Intensive*: Independent of the size of the system
($T, p, \bar{V} = \frac{V}{n}, \dots$)

The State of a System at Equilibrium:

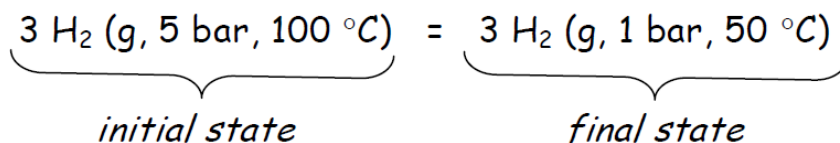
- Defined by the collection of all macroscopic properties that are described by *State* variables (p, n, T, V, \dots)
[INDEPENDENT of the HISTORY of the SYSTEM]
- For a one-component System, all that is required is " n " and 2 variables. All other properties then follow.

$$V = f(n, p, T) \quad \text{or} \quad p = g(n, V, T)$$

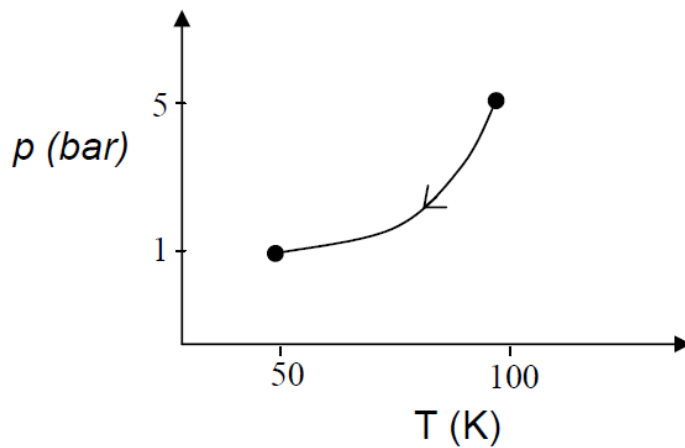
- Notation:

Change of State: (Transformations)

- Notation:



- Path*: Sequence of intermediate states



• *Process:* Describes the Path

- Reversible (always in Equilibrium)
- Irreversible (defines direction of time)
- Adiabatic (no heat transfer between system and surroundings)
- Isobaric (constant pressure)
- Isothermal (constant temperature)

TEMPERATURE

Temperature is commonly measured with liquid-in-glass thermometers, where in the liquid expands when heated. Thus a uniform tube partially filled with mercury, alcohol, or some other fluid, can indicate degree of "hotness" simply by the length of the fluid column. However, numerical values are assigned to the various degrees of hotness by arbitrary definition.

1. Celsius scale: ($^{\circ}\text{C}$) formally called centigrade

2. Absolute temperature

a. Kelven scale

b. Rankin scale

$$T_{(K)} = T_{(^{\circ}\text{C})} + 273.15$$

$$T_{(^{\circ}\text{F})} = 1.8 T_{(^{\circ}\text{C})} + 32$$

$$T_{(R)} = T_{(^{\circ}\text{F})} + 459.67$$

$$T_{(R)} = 1.8 T_{(K)}$$

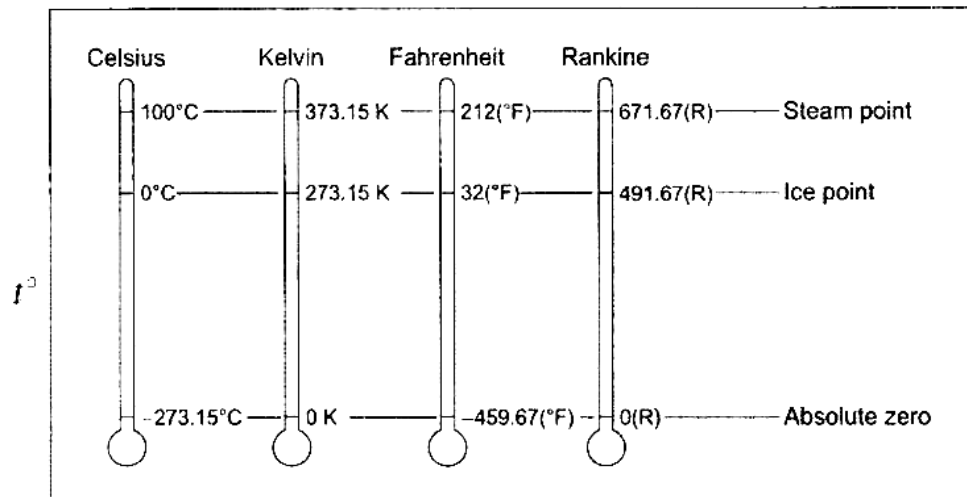


Figure 1.1 Relations among temperature scales

The zeroth law of thermodynamics :

The zeroth law of thermodynamics states that two bodies are in thermal equilibrium if both have the same temperature reading, even if they are not in contact.

EX/ The deep body temperature of a healthy person is 37°C. What is it in kelvins and rankin ?

SOL/

A temperature is given in °C. It is to be expressed in K.

Analysis The Kelvin scale is related to Celsius scale by

$$T_{(K)} = T_{(°C)} + 273$$

$$\text{Thus, } T_{(K)} = T_{(°C)} + 273$$

$$T_{(K)} = 37°C + 273 = 310 \text{ K}$$

$$T_{(R)} = 1.8 T_{(K)}$$

Ideal Gases

Boyle's Law and the Kelvin scale

$$\lim_{p \rightarrow 0} (p\bar{V})_T = \left[\frac{\lim_{p \rightarrow 0} (p\bar{V})_{tp}}{273.16} \right] T \equiv \bar{R}T \quad \text{valid for all gases for } p \rightarrow 0$$

define
the "gas constant"

An ideal gas obeys the expression $p\bar{V} = \bar{R}T$ at all pressures
(\Rightarrow the gas molecules do not interact)

$$PV = n\bar{R}T, \quad P\bar{v} = \bar{R}T$$

This is an example of an equation of state

$$V = f(n, p, T)$$

in which n is the number of kmol of gas, or

$$n = \frac{m}{M} \frac{\text{kg}}{\text{kg/kmol}}$$

Mass m is simply the amount of matter; molar mass M is the mass of one mole in grams or the mass of one kmol in kilograms.

\bar{R} is the universal gas constant, the value of which is, for any gas,

$$\bar{R} = 8.3145 \frac{\text{kJ}}{\text{kmol K}} = 8.3145 \frac{\text{kJ}}{\text{kmol K}}$$

where, $R = \frac{\bar{R}}{M}$

thus, $PV = mRT$

Boyles Law (T const) Charles Law (v const) Gay-Lussacs Law (P const)

$$\frac{p_2}{p_1} = \frac{v_1}{v_2}$$

$$\frac{p_2}{p_1} = \frac{T_2}{T_1}$$

$$\frac{v_2}{v_1} = \frac{T_2}{T_1}$$

EX/ A tank has a volume of 0.5 m^3 and contains 10 kg of an ideal gas having a molecular mass of 24. The temperature is 25°C . What is the pressure?

SOL/

The gas constant is determined first:

$$R = \frac{\bar{R}}{M} = \frac{8.3145 \text{ kJ mol}^{-1} \text{ K}^{-1}}{24 \text{ kg/kmol}} = 0.34644 \text{ kJ kg}^{-1} \text{ K}^{-1}$$

We now solve for P :

$$P = \frac{mRT}{V} = \frac{10 \text{ kg} \times 0.34644 \text{ kJ kg}^{-1} \text{ K}^{-1} \times 298.2 \text{ K}}{0.5 \text{ m}^3} = 2066 \text{ kPa}$$

EX/ A tank has a volume of 15 ft^3 and contains 20 lbm of an ideal gas having a molecular mass of 24. The temperature is 80°F . What is the pressure?

Sol/

The gas constant is determined first:

$$R = \frac{\bar{R}}{M} = \frac{1545 \text{ ft lbf/lb mol R}}{24 \text{ lbm/lb mol}} = 64.4 \text{ ft lbf/lbm R}$$

We now solve for P :

$$P = \frac{mRT}{V} = \frac{20 \text{ lbm} \times 64.4 \text{ ft lbf/lbm R} \times 540 \text{ R}}{144 \text{ in.}^2/\text{ft}^2 \times 15 \text{ ft}^3} = 321 \text{ lbf/in.}^2$$

Equations of state

IDEAL GAS LAW: $pV = nRT \rightarrow p\bar{V} = RT$

Mixture of ideal gases comprising n_i moles of each

$$p_i = \frac{n_i RT}{V} \leftarrow \text{Partial pressure of } i^{\text{th}} \text{ gas}$$

$$p = p_{\text{Total}} = \sum_i p_i ; \quad X_i = \frac{n_i}{n} \text{ mole fraction of } i^{\text{th}} \text{ gas}$$

$$p_i = \frac{n_i}{n} p = X_i p \quad \text{Dalton's Law}$$

Real Gases

-- do not necessarily obey ideal gas law

(a) Compressibility factor

$$p\bar{V} = ZRT \quad Z = \frac{\bar{V}_{real}}{\bar{V}_{ideal}}$$

High T \Rightarrow Repulsions dominate $Z > 1$ $\bar{V}_{real} > \bar{V}_{ideal}$

Low T \Rightarrow Attractions dominate $Z < 1$ $\bar{V}_{real} < \bar{V}_{ideal}$

reduced pressure $= P_r = \frac{P}{P_c}$, $P_c =$ critical pressure

reduced temperature $= T_r = \frac{T}{T_c}$, $T_c =$ critical temperature

(b) Virial Expansion

generally neglect

$$\frac{p\bar{V}}{RT} = Z(T) = 1 + \frac{B(T)}{\bar{V}} + \frac{C(T)}{\bar{V}^2} + \dots$$

As $p \rightarrow 0, \bar{V} \rightarrow \infty, \Rightarrow$ ideal gas $B = 0 \Rightarrow$ ideal gas
(neglect C and higher order terms)

(c) van der Waals Equation of state

only two parameters, derived from molecular concepts

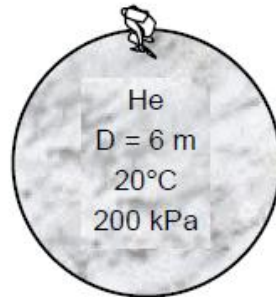
- First assume "hard sphere" molecules

$$p\bar{V} = RT \quad \text{becomes} \quad p(\bar{V} - b) = RT$$

- Now put in attraction

So $p = \left(\frac{RT}{\bar{V} - b} \right)$ becomes $p = \left(\frac{RT}{\bar{V} - b} \right) - \frac{a}{\bar{V}^2}$ $P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$

EX/ A spherical balloon with a diameter of 6 m is filled with helium at 20°C and 200 kPa. Determine the mole number and the mass of the helium in the balloon (molar mass of helium is 4.0 kg/kmol)?



SOL/

The volume of the sphere is

$$V = \frac{4}{3} \pi r^3 = \frac{4}{3} \pi (3 \text{ m})^3 = 113.1 \text{ m}^3$$

Assuming ideal gas behavior, the mole numbers of He is determined from

$$N = \frac{PV}{R_u T} = \frac{(200 \text{ kPa})(113.1 \text{ m}^3)}{(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(293 \text{ K})} = \mathbf{9.28 \text{ kmol}}$$

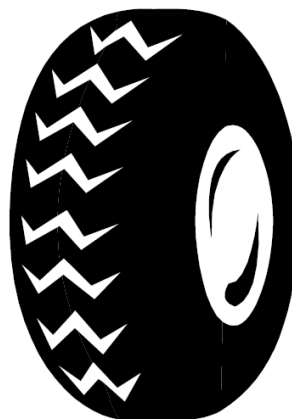
Then the mass of He can be determined from

$$m = NM = (9.28 \text{ kmol})(4.0 \text{ kg/kmol}) = \mathbf{37.15 \text{ kg}}$$

EX/ Air in an automobile tire is initially at -10°C and 190 kPa. After the automobile is driven awhile, the temperature gets up to 10°C . Find the new pressure. You must make one assumption on your own.

SOL/ Assume constant volume and that air is an ideal gas

$$\begin{aligned} P_2 &= P_1 \times T_2/T_1 \\ &= 190 \times \frac{283.15}{263.15} = \mathbf{204.4 \text{ kPa}} \end{aligned}$$



EX/ A cylindrical gas tank 1 m long, inside diameter of 20 cm, is evacuated and then filled with carbon dioxide gas at 20° C. To what pressure should it be charged if there should be 1.2 kg of carbon dioxide? (using tables)

SOL/

Assume CO₂ is an ideal gas, table : R = 0.1889 kJ/kg K

$$V_{\text{cyl}} = A \times L = \frac{\pi}{4}(0.2)^2 \times 1 = 0.031416 \text{ m}^3$$

$$P V = mRT \quad \Rightarrow \quad P = \frac{mRT}{V}$$

$$\Rightarrow P = \frac{1.2 \text{ kg} \times 0.1889 \text{ kJ/kg K} \times (273.15 + 20) \text{ K}}{0.031416 \text{ m}^3} = \mathbf{2115 \text{ kPa}}$$

EX/ Carbon dioxide at 60°C is pumped at a very high pressure 10 MPa into an oil well to reduce the oil viscosity for better oil flow. What is its compressibility?(using tables)

SOL/ From table : v = 0.00345 m³/kg

$$Z = Pv/RT = \frac{10\,000 \text{ kPa} \times 0.00345 \text{ m}^3/\text{kg}}{0.1889 \text{ kJ/kg-K} \times 333 \text{ K}} = \mathbf{0.55}$$

EX/A 1 m³ rigid tank has propane at 100 kPa, 300 K and connected by a valve to another tank of 0.5 m³ with propane at 250 kPa, 400 K. The valve is opened and the two tanks come to a uniform state at 325 K. What is the final pressure? (using tables)

Sol/ Propane is an ideal gas (P << P_c) with R = 0.1886 kJ/kgK from Tables.

$$m_A = \frac{P_A V_A}{RT_A} = \frac{100 \times 1}{0.1886 \times 300} = 1.7674 \text{ kg}$$

$$m_B = \frac{P_B V_B}{RT_B} = \frac{250 \times 0.5}{0.1886 \times 400} = 1.6564 \text{ kg}$$

$$V_2 = V_A + V_B = 1.5 \text{ m}^3$$

$$m_2 = m_A + m_B = 3.4243 \text{ kg}$$

$$P_2 = \frac{m_2 R T_2}{V_2} = \frac{3.4243 \times 0.1886 \times 325}{1.5} = \mathbf{139.9 \text{ kPa}}$$