

# Lecture 2

## Laws of Perfect Gases

- Definition of gases, explanation of perfect gas laws – Boyle's law, Charle's law, Avagadro's law, Universal gas constant, Characteristic gas constants, derivation Specific heat at constant pressure, specific heat at constant volume of gas, derivation of an expression for specific heats with characteristics, simple problems on gas equation

# About gases

- A gas is a form of matter characterized by its lack of a definite shape and volume.
- Gases exhibit lower density compared to solids and liquids, and their particles possess substantial kinetic energy while displaying minimal attraction to each other.
- The presence of significant empty space between particles allows gases to diffuse, spreading out uniformly within the container.
- As one of the three fundamental states of matter, gases display unique properties distinct from those of liquids and solids



# About gases

- Gases have mass
- Gases exert pressure
- Gases can expand to take up large volumes
- Gases can be compressed to fit in small volumes

# Perfect gas laws

- A perfect gas (ideal gas) is a gas that obeys the ideal gas law fully in its physical behavior.
- It connects the pressure of the gas, the amount of space occupied by the gas number of gas molecules, as well as the absolute temperature of the gas.
- In the entire universe, there is no such gas that possesses the properties of a perfect gas.
- In short, the ideal gas has the following relation;

$$pv=nRT$$

*p* is the pressure

*v* is the volume

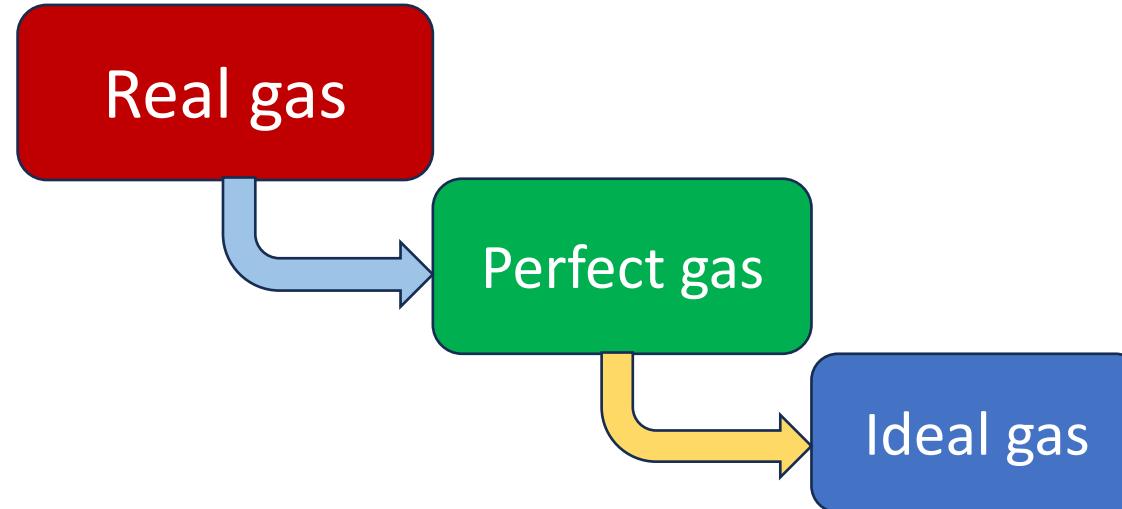
*n* is the amount of substance (moles)

*T* is temperature

*R* is the universal gas constant 8.31 J/K.mol

# Gas laws

- At very low pressure and high temperature, all real gases and vapour approaches ideal gas behavior is called perfect gas.



- The ideal gas law, despite its limitations, is a good approximation of the behavior of many gasses in several conditions.

# Gas laws

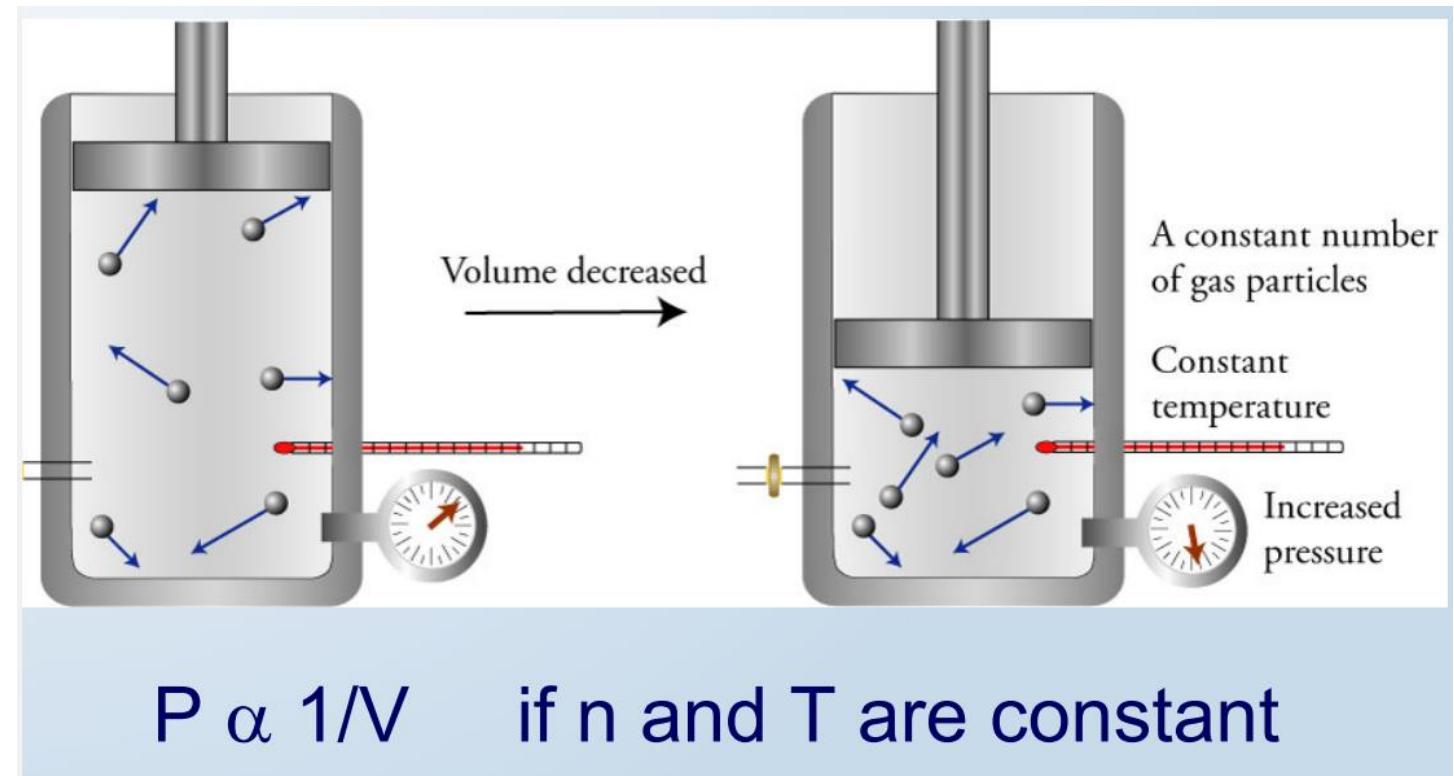
- The following are the objectives of gas law properties,
  - 1) describe the relationship between them,
  - 2) describe a simple system that could be used to demonstrate the relationship, and
  - 3) explain the reason for the relationship.

# Gas laws

## Boyle's law

- The Volume of a given Mass of a Gas varies inversely as its absolute Pressure, provided the **moles** and **Temperature** remains constant.

$$V \propto 1/P$$

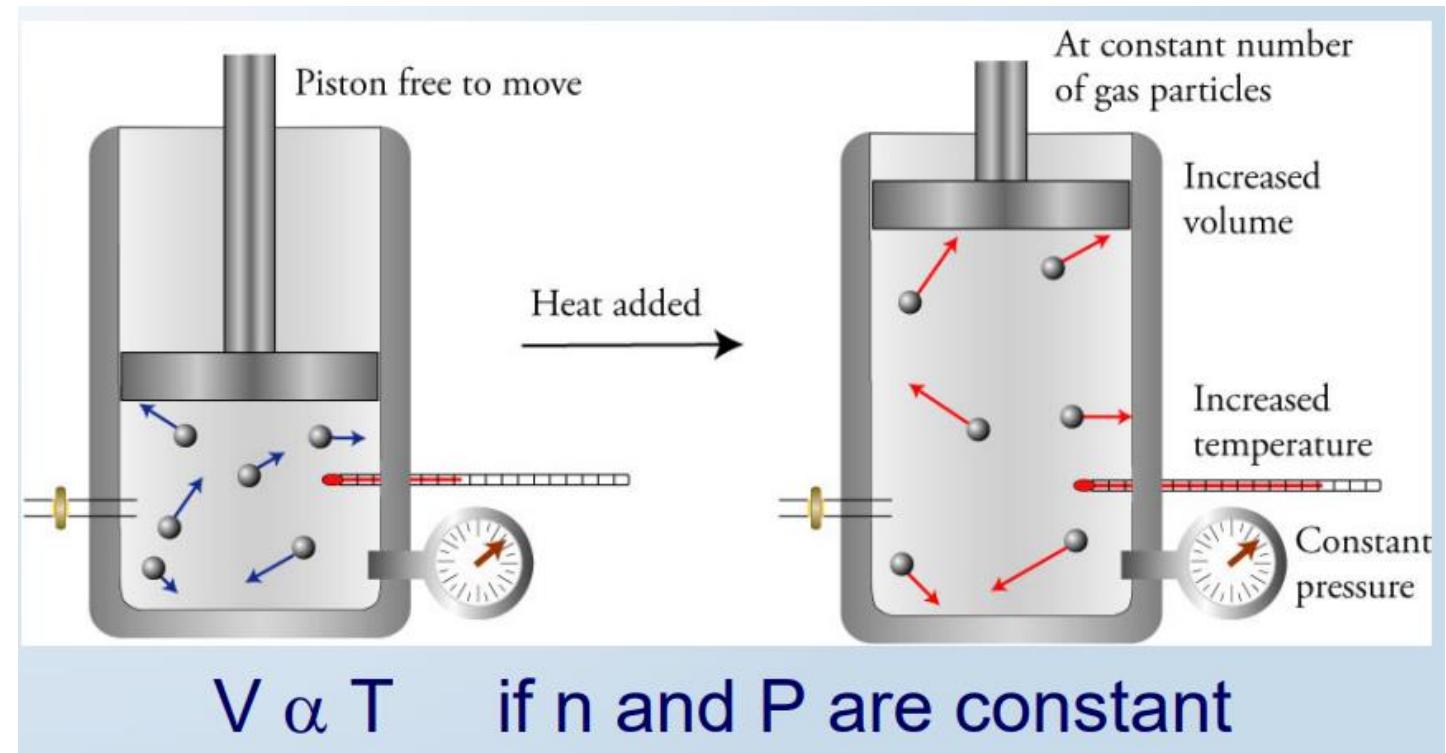


# Gas laws

## Charles's law

- The volume of a given Mass of a Gas varies directly as its absolute Temperature provided the **moles** and **Pressure** is kept constant.

$$V \propto T$$

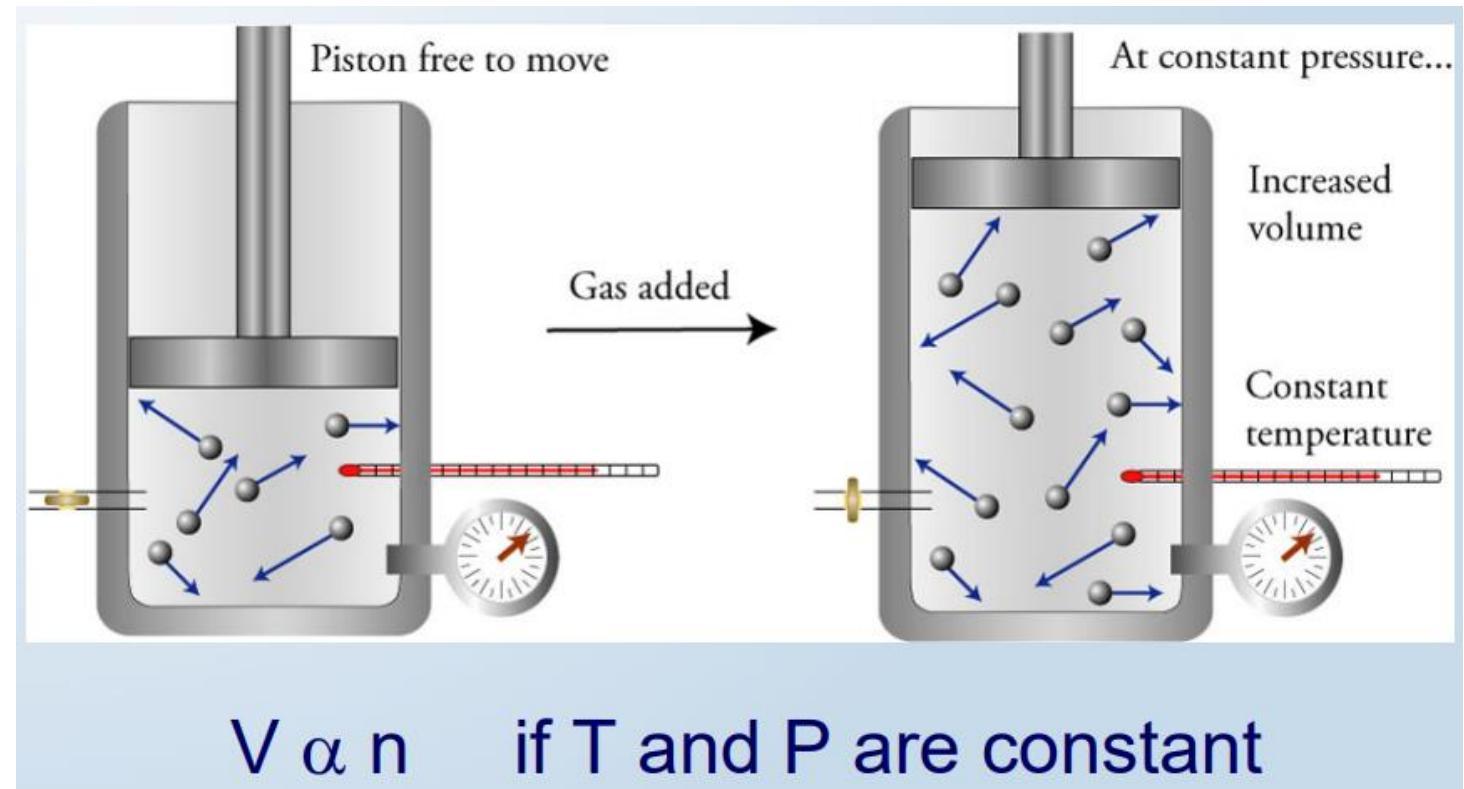


# Gas laws

## Avogadro's Law

- For a given mass of an ideal gas, the volume and amount (moles) of the gas are directly proportional if the **temperature and pressure** are constant.

$$V \propto n$$



# Example 1

You have 10mol of a gas at 30°C, occupying a container which is 0.5Lt in size. What is the pressure of this gas in atmospheres?

Given data

$$n=10\text{mol}$$

$$T=30^\circ\text{C}$$

$$V=0.5\text{Lt}$$

$$P=?$$

$$T = 30^\circ\text{C}$$

$$= 30^\circ\text{C} + 273$$

$$= 303 \text{ K}$$

Values of Gas Constant

$$\bar{R} = 0.0827 \frac{\text{atm} \cdot \text{L}}{\text{Mol} \cdot \text{K}}$$

Substitute the values now

$$P \times 0.5 \text{ L} = 10 \text{ mol} \times 0.0827 \frac{\text{atm} \cdot \text{L}}{\text{Mol} \cdot \text{K}} \times 303 \text{ K}$$

$$P = 10 \text{ mol} \times 0.0827 \frac{\text{atm} \cdot \text{L}}{\text{Mol} \cdot \text{K}} \times 303 \text{ K} / 0.5 \text{ L}$$

**Ans is P = ?:**

**P = 501.2 atm**

Ideal Gas equation

$$PV = n \bar{R} T$$

Temperature in Kelvin

Universal Gas Constant

Number of moles

Volume of gas

Pressure

$$\bar{R} = 8.31441 \text{ KJ/K.mol K}$$

## Example 2

What is the molar mass of gas which has a density of 1.83g/Lt measured at 27°C and 0.538atm? (R=0.0821Lt-atm/K-mol).

Given data

$$V=1.00\text{Lt}$$

$$\text{mass}=1.83\text{g}$$

$$T=27^\circ\text{C}=300\text{K}$$

$$R=0.0821\text{Lt-atm/K-mol}$$

$$n=?$$

$$M, \text{ molar mass}=? \text{ g/mol}$$

$$n = \frac{PV}{RT} = \frac{0.538 \text{ atm} \times 1.00 \text{ L}}{0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300.1 \text{ K}} = 0.0218 \text{ mol}$$

$$M = \frac{\text{#grams}}{\text{# mol}} = \frac{1.83 \text{ g}}{0.0218 \text{ mol}} = 83.9 \text{ g/mol}$$

# Example 3

A hot air balloon holds 30kg of helium. What is the volume of the balloon if the final pressure is 1.2atm and the temperature 22°C?

Given data

$$P=1.2\text{atm}$$

$$n = \frac{\text{mass}}{\text{molar mass}} = 30\text{kg} \times \frac{1000\text{g}}{1\text{kg}} \times \frac{1\text{mol He}}{4\text{g He}}$$

$$T=22^\circ\text{C}=295\text{K}$$

$$=7500\text{mol}=7.5\times 10^3 \text{ mol}$$

$$R=0.0821\text{Lt-atm/K-mol} \quad V=?$$

mass=30kg of He

Molar mass  $M=4\text{g/mol}$

$$PV = nRT$$

$$V = \frac{nRT}{P} = \frac{7.50 \times 10^3 \cancel{\text{mol}} \times .0821 \cancel{\text{L atm K}^{-1}} \cancel{\text{mol}^{-1}} \times 295 \cancel{K}}{1.20 \cancel{\text{atm}}}$$

$$V = 151,371.875 \text{ L} = 1.51 \times 10^5 \text{ L}$$

# Gas constant $R$

Gas Constant	Universal Gas Constant $R$
<ol style="list-style-type: none"><li>1. SI unit is <math>\text{J kg}^{-1}\text{K}^{-1}</math>.</li><li>2. Gas constant depends on mass.</li><li>3. Number of moles of gas <math>\mu = \frac{m}{M}</math> where <math>M</math> is molar mass of gas.</li><li>4. <math>r = \left(\frac{m}{M}\right)R</math> in the equation <math>PV = rT</math> and <math>V</math> is volume of <math>\mu</math> moles of gas.</li><li>5. <math>r = \left(\frac{m}{M}\right) \times 8.314 \text{ J kg}^{-1} \text{ K}^{-1}</math>.</li></ol>	<ol style="list-style-type: none"><li>1. S.I unit of measurement is <math>\text{J mole}^{-1} \text{ K}^{-1}</math>.</li><li>2. Universal constant is with respect to a fixed mass of 1 mole of any gas.</li><li>3. Number of moles of gas is always for <math>\mu = 1</math>.</li><li>4. <math>R = \frac{PV}{T}</math> where <math>V</math> is volume of 1 mole of gas.</li><li>5. <math>R = 8.314 \text{ J mole}^{-1} \text{ K}^{-1}</math>.</li></ol>

# Gas constant $R$

Gas	Molar Weight ( M)Kg/Kmol	Gas Constant (R )KJ/KgK
Air	28.97	0.287
Nitrogen	28.01	0.297
Oxygen	32	0.260
Hydrogen	2.016	4.124
Helium	4.004	2.077
Carbon dioxide	44.01	0.189
Steam	18.02	0.461

# Specific Heat Capacity

- Specific heat capacity, is a fundamental thermodynamic property denoted as “c,” quantifies the energy required to elevate the temperature of a unit mass of a substance by a given temperature increment.
- It is typically expressed in units of Joules per kilogram per Kelvin ( $J/(kg \cdot K)$ ) in the International System of Units (SI) or in calories per gram per degree Celsius ( $Cal/(g \cdot ^\circ C)$ ) in some contexts.
- This property characterizes a material's inherent capacity to absorb, store, and release thermal energy.

# Specific Heat Capacity

- The specific heat of a substance can be determined through an isochoric (constant-volume) or an isobaric (constant-pressure) process.
- These specific heats are denoted as  $c_v$  and  $c_p$ , respectively, and they are inherent characteristics of a material.
- They play a pivotal role in computing alterations in a substance's specific internal energy (U) and specific enthalpy (H) in processes encompassing ideal gases, liquids, and solids.
- These properties offer a framework for assessing energy content changes in a substance under various thermodynamic conditions, thereby aiding in comprehending and quantifying matter's thermal behavior.

# Specific Heat ( $c_v$ & $c_p$ )

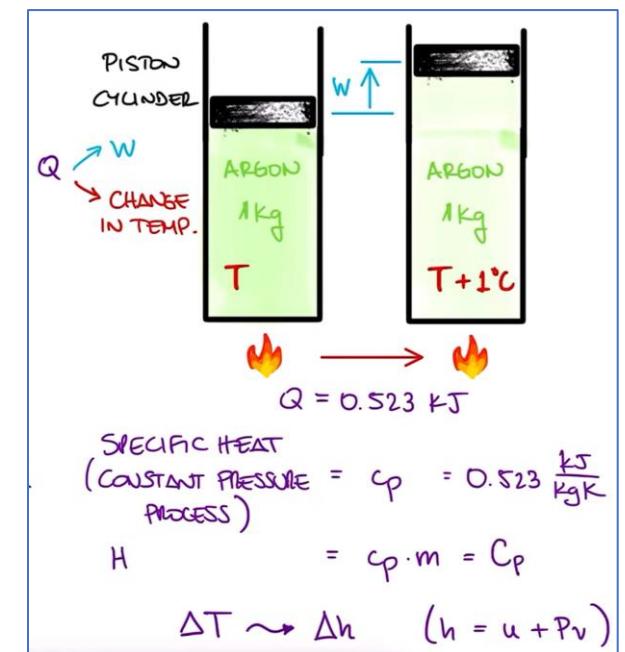
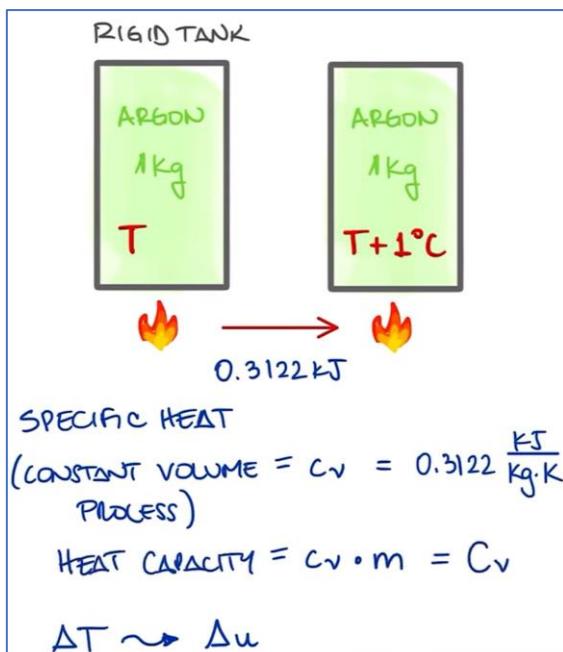
- Specific heat, represents the amount of energy needed to increase the temperature of a single unit mass (1 kg) of a material by one degree (1°C or 1 K) within an isochoric process. In mathematical terms, it is defined as:

$$Q = mc\Delta T$$

$$\frac{Q}{m} = c\Delta T \Rightarrow q$$

$$\frac{q}{\Delta T} = c$$

The  $c$  will change based on what is held constant;  $c_v$  @ constant  $v$ , and  $c_p$  @constant  $p$



# Specific Heat ( $c_v$ & $c_p$ )

Consider the 1<sup>st</sup> law of thermodynamics

$$\Delta U = Q - W$$

If mass is divided on both sides and take a derivatives

$$du = \delta q - \delta w$$

But  $\delta w = pdv$

$$\delta q = \delta u + pdv$$

The symbol for partial derivatives ( $\delta$ ) is used in  $q$  &  $w$  because are not properties

# Specific Heat ( $c_v$ & $c_p$ )

Internal energy

$$u = u(T, v)$$

Its total derivatives based on the impact of respective variable is given as;

$$du = \frac{\partial u}{\partial T} dT + \frac{\partial u}{\partial v} dv$$

$$du = \left[ \frac{\partial u}{\partial T} \right]_v dT + \left[ \frac{\partial u}{\partial v} \right]_T dv$$

From the 1<sup>st</sup> law of thermodynamics

$$\delta q = \partial u + pdv$$

$$\delta q = \left[ \frac{\partial u}{\partial T} \right]_v dT + \left[ \frac{\partial u}{\partial v} \right]_T dv + pdv$$

0  
0  
Const. volume process

$$\frac{\delta q}{dT} = \left[ \frac{\partial u}{\partial T} \right]_v = c_v$$

← Const. volume specific heat

Enthalpy

$$h = h(T, p)$$

Its total derivatives based on the impact of respective variable is given as;

$$dh = \frac{\partial h}{\partial T} dT + \frac{\partial h}{\partial p} dp$$

$$dh = \left[ \frac{\partial h}{\partial T} \right]_p dT + \left[ \frac{\partial h}{\partial p} \right]_T dp$$

From the 1<sup>st</sup> law of thermodynamics

$$\delta q = \partial u + pdv$$

But  $u = h - pv$

$$du = dh - pdv - vdp$$

Therefore  $\delta q = dh - pdv - vdp + pdv$

$$\delta q = \left[ \frac{\partial h}{\partial T} \right]_p dT + \left[ \frac{\partial h}{\partial p} \right]_T dp - vdp$$

0  
0  
Const. pressure process

$$\frac{\delta q}{dT} = \left[ \frac{\partial h}{\partial T} \right]_p = c_p$$

← Const. pressure specific heat

# Ideal Gas and relationship between $C_p$ and $C_v$

- From the ideal gas equation  $pv = nRT$
- For specific gas  $pv = RT$
- Recall  $u = h - pv$
- Therefore

$$\begin{aligned}u &= h - RT \\ \Rightarrow du &= dh - RdT \\ c_v dT &= c_p dT - RdT \\ c_v &= c_p - R\end{aligned}.$$

The specific heat ratio  $\frac{c_p}{c_v} = \gamma$

$\gamma$  varies with temperature, but this variation is very mild then  
 $\gamma$  =constant.

$\gamma = 1.4$  for diatomic gases (like air)

$\gamma = 1.667$  for noble gases (monoatomic gases)

## Example 4

Air at 300 K and 200 kPa is heated at constant pressure to 600 K. Determine the change in internal energy of air per unit mass, using

- (a) data from the air table (Table A-17),
- (b) the functional form of the specific heat (Table A-2c), and
- (c) the average specific heat value (Table A-2b).

**Solution** The internal energy change of air is to be determined in three different ways.

**Assumptions** At specified conditions, air can be considered to be an ideal gas since it is at a high temperature and low pressure relative to its critical-point values.

**Analysis** The internal energy change  $\Delta u$  of ideal gases depends on the initial and final temperatures only, and not on the type of process. Thus, the following solution is valid for any kind of process.

(a) One way of determining the change in internal energy of air is to read the  $u$  values at  $T_1$  and  $T_2$  from Table A-17 and take the difference:

$$u_1 = u @ 300 \text{ K} = 214.07 \text{ kJ/kg}$$

$$u_2 = u @ 600 \text{ K} = 434.78 \text{ kJ/kg}$$

Thus,

$$\Delta u = u_2 - u_1 = (434.78 - 214.07) \text{ kJ/kg} = \mathbf{220.71 \text{ kJ/kg}}$$

(b) The  $\bar{c}_p(T)$  of air is given in Table A-2c in the form of a third-degree polynomial expressed as

$$\bar{c}_p(T) = a + bT + cT^2 + dT^3$$

where  $a = 28.11$ ,  $b = 0.1967 \times 10^{-2}$ ,  $c = 0.4802 \times 10^{-5}$ , and  $d = -1.966 \times 10^{-9}$ . From Eq. 4-30,

$$\bar{c}_v(T) = \bar{c}_p - R_u = (a - R_u) + bT + cT^2 + dT^3$$

From Eq. 4-25,

$$\Delta \bar{u} = \int_{T_1}^{T_2} \bar{c}_v(T) \, dT = \int_{T_1}^{T_2} [(a - R_u) + bT + cT^2 + dT^3] \, dT$$

Performing the integration and substituting the values, we obtain

$$\Delta \bar{u} = 6447 \text{ kJ/kmol}$$

The change in the internal energy on a unit-mass basis is determined by dividing this value by the molar mass of air (Table A-1):

$$\Delta u = \frac{\Delta \bar{u}}{M} = \frac{6447 \text{ kJ/kmol}}{28.97 \text{ kg/kmol}} = \mathbf{222.5 \text{ kJ/kg}}$$

which differs from the tabulated value by 0.8 percent.

(c) The average value of the constant-volume specific heat  $c_{v,\text{avg}}$  is determined from Table A-2b at the average temperature of  $(T_1 + T_2)/2 = 450 \text{ K}$  to be

$$c_{v,\text{avg}} = c_v @ 450 \text{ K} = 0.733 \text{ kJ/kg} \cdot \text{K}$$

Thus,

$$\begin{aligned} \Delta u &= c_{v,\text{avg}}(T_2 - T_1) = (0.733 \text{ kJ/kg} \cdot \text{K})[(600 - 300) \text{ K}] \\ &= 220 \text{ kJ/kg} \end{aligned}$$

## Example 4

A piston–cylinder device initially contains  $0.5 \text{ m}^3$  of nitrogen gas at  $400 \text{ kPa}$  and  $27^\circ\text{C}$ . An electric heater within the device is turned on and is allowed to pass a current of  $2 \text{ A}$  for  $5 \text{ min}$  from a  $120\text{-V}$  source. Nitrogen expands at constant pressure, and a heat loss of  $2800 \text{ J}$  occurs during the process. Determine the final temperature of nitrogen.

**Solution** Nitrogen gas in a piston–cylinder device is heated by an electric resistance heater. Nitrogen expands at constant pressure while some heat is lost. The final temperature of nitrogen is to be determined.

**Assumptions** 1 Nitrogen is an ideal gas since it is at a high temperature and low pressure relative to its critical-point values of  $-147^{\circ}\text{C}$ , and 3.39 MPa. 2 The system is stationary and thus the kinetic and potential energy changes are zero,  $\Delta\text{KE} = \Delta\text{PE} = 0$  and  $\Delta E = \Delta U$ . 3 The pressure remains constant during the process and thus  $P_2 = P_1$ . 4 Nitrogen has constant specific heats at room temperature.

**Analysis** We take the contents of the cylinder as the *system* (Fig. 4–31). This is a *closed system* since no mass crosses the system boundary during the process. We observe that a piston–cylinder device typically involves a moving boundary and thus boundary work,  $W_b$ . Also, heat is lost from the system and electrical work  $W_e$  is done on the system.

First, let us determine the electrical work done on the nitrogen:

$$W_e = \mathbf{VI} \Delta t = (120 \text{ V})(2 \text{ A})(5 \times 60 \text{ s}) \left( \frac{1 \text{ kJ/s}}{1000 \text{ VA}} \right) = 72 \text{ kJ}$$

The mass of nitrogen is determined from the ideal-gas relation:

$$m = \frac{P_1 V_1}{R T_1} = \frac{(400 \text{ kPa})(0.5 \text{ m}^3)}{(0.297 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(300 \text{ K})} = 2.245 \text{ kg}$$

Under the stated assumptions and observations, the energy balance on the system can be expressed as

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\substack{\text{Net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{\text{system}}}_{\substack{\text{Change in internal, kinetic,} \\ \text{potential, etc., energies}}}$$

$$W_{e,\text{in}} - Q_{\text{out}} - W_{b,\text{out}} = \Delta U$$

$$W_{e,\text{in}} - Q_{\text{out}} = \Delta H = m(h_2 - h_1) = mc_p(T_2 - T_1)$$

since  $\Delta U + W_b \equiv \Delta H$  for a closed system undergoing a quasi-equilibrium expansion or compression process at constant pressure. From Table A-2a,  $c_p = 1.039 \text{ kJ/kg} \cdot \text{K}$  for nitrogen at room temperature. The only unknown quantity in the previous equation is  $T_2$ , and it is found to be

$$72 \text{ kJ} - 2.8 \text{ kJ} = (2.245 \text{ kg})(1.039 \text{ kJ/kg} \cdot \text{K})(T_2 - 27^\circ\text{C})$$

$$T_2 = \mathbf{56.7^\circ\text{C}}$$