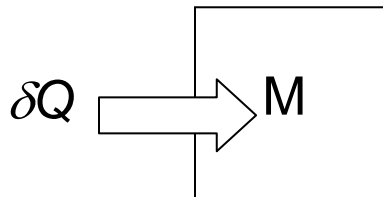## Specific Heat

Macroscopically, **specific heat c** , is an intensive property that represents the amount of heat that needs to be added to 1 kg of material to raise its temperature by 1^oK

For example : $c = \dfrac{\delta Q}{MdT}$ units : $\dfrac{KJ}{kg \cdot {}^oK}$

The value of c depends on the process of heat addition

For constant volume heat addition:

$$\delta Q \Longrightarrow \boxed{M}$$

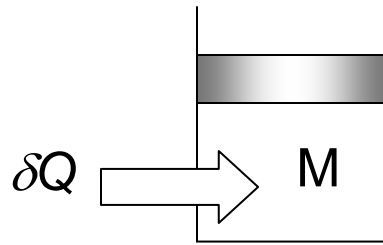$$\Delta U = \delta Q - \delta W$$

$$Mdu = \delta Q - \cancel{pdV}$$

Hence define specific heat at constant volume as

$$c = \dfrac{\delta Q}{MdT} = \dfrac{Mdu}{MdT} = \left.\dfrac{du}{dT}\right|_{V\,const} = c_V \qquad \boxed{du = c_V dT}$$

In general c_v depends on P and T, so

$$\boxed{u_2 - u_1 = \int_1^2 du = \int_1^2 c_V(P,T)dT}$$

For constant pressure heat addition:

$$\Delta U = \delta Q - W$$
$$Mdu = \delta Q - pdV$$
$$Mdu = \delta Q - p(Mdv)$$
$$\delta Q = M(du + Pdv)$$

Define new property, **enthalpy h**

$$\boxed{h = u + Pv} \rightarrow dh = du + Pdv + vdP$$

For constant P process dP=0, so $dh = du + Pdv$

Substituting into the definition for c

$$c = \frac{\delta Q}{MdT} = \frac{M(du + Pdv)}{Mdt} = \frac{dh}{dT}\bigg|_{\text{P const}} = c_P \qquad \boxed{dh = c_P dT}$$

In general c_P also depends on P and T, so

$$\boxed{h_2 - h_1 = \int_1^2 dh = \int_1^2 c_P(P,T)dT}$$

Ideal Gas Assumption

For an ideal gas c_V and c_P only vary with T, not P

$$u_2 - u_1 = \int_1^2 c_v(T)dT$$
$$h_2 - h_1 = \int_1^2 c_P(T)dT$$

Need absolute u and h. Set T_2 to T and T_1 to T_{ref}

$$h_2 - h_1 = h(T) - h(T_{ref}) = \int_{T_{ref}}^T c_P(T)dT$$

Take $T_{ref} = 0$ (absolute zero temperature) where h=0

$$\boxed{\begin{array}{l} h(T) = \int_0^T c_P(T)dT \\ \bar{h}(T) = \int_0^T \bar{c}_P(T)dT \end{array}}$$

for an ideal gas $\quad pv = RT$

$$\therefore h = u + pv = u + RT \rightarrow u = h - RT$$

$$\boxed{\begin{array}{l} u(T) = \int_0^T c_P(T)dT - RT \\ \bar{u}(T) = \int_0^T \bar{c}_P(T)dT - \bar{R}T \end{array}}$$

c_p values are tabulated in Table A-20 and Table A-21 gives an empirical relation for $(\bar{c}_p / \bar{R})$ as a function of T for various gases.

Enthalpy and Internal energy as a function of T for air is given in Table A-22, and for other gases in A-23.

Get c_V from c_P differentiate $h = u + RT$ with respect to T

$$\frac{dh}{dT} = \frac{du}{dT} + R \rightarrow \boxed{c_P(T) = c_V(T) + R}$$

$$\frac{d\bar{h}}{dT} = \frac{d\bar{u}}{dT} + R \rightarrow \boxed{\bar{c}_P(T) = \bar{c}_V(T) + \bar{R}}$$

Note :   Since R > 0 and $c_V > 0$ $\rightarrow$ $c_p > c_V$

The **specific heat ratio** k is commonly used, for ideal gas

$$\boxed{k(T) = \frac{c_P}{c_V}} \quad \text{since } c_P > c_V \rightarrow k > 1 \quad \text{see Table A - 20}$$

For a substance with molar mass μ if you know k at a specific temperature can get c_p and c_V

$$c_P(T) = c_V(T) + R \qquad\qquad c_P(T) = c_V(T) + R$$

$$\frac{c_P(T)}{c_V(T)} = 1 + \frac{R}{c_V(T)} \qquad\qquad c_P(T) = \frac{R}{K(T)-1} + R$$

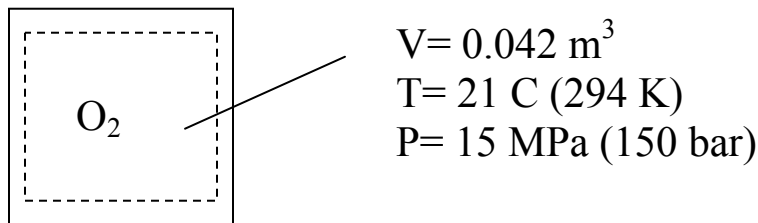$$\boxed{c_V(T) = \frac{R}{K(T)-1}} \qquad\qquad \boxed{c_P(T) = \frac{K(T)R}{K(T)-1}}$$

Example:

A tank contains 0.042 m³ of oxygen (O_2) at 21C and 15 MPa.
Determine the mass of the oxygen, in kg, using
  a) the compressibility chart
  b) ideal gas model
Comment on the applicability of the ideal gas model

V= 0.042 m³
T= 21 C (294 K)
O_2
P= 15 MPa (150 bar)

a) From table A-1for oxygen: molar mass µ= 32 kg/kmol,
T_c= 126K, P_c=50.5 bar

$$P_R = \frac{P}{P_c} = \frac{150 \text{ bar}}{50.5 \text{ bar}} = 2.97 \; ; \; T_R = \frac{T}{T_c} = \frac{294 \text{ K}}{126 \text{ K}} = 1.91$$

From the Generalized Compressibility Chart $Z \approx 0.92$

$$v = \frac{ZRT}{P} = \frac{0.92(8314/32 \text{ J/kg} \cdot \text{K})(294 \text{K})}{150 \text{x} 10^5 \text{ N/m}^2} = 0.0047 \text{ kg/m}^3$$

$$M = \frac{V}{v} = \frac{0.042 \text{ m}^3}{0.0047 \text{ /m}^3 \text{/kg}} = \boxed{8.94 \text{ kg}}$$

b) Assuming ideal gas

$$M = \frac{PV}{RT} = \frac{(150 \times 10^5 \text{ N/m}^2)(0.042 \text{m}^3)}{(8314/32 \text{ J/kg} \cdot \text{K})(294 \text{K})} = \boxed{8.24 \text{ kg}}$$

Assuming the mass obtained from the chart is correct, the ideal gas model under predicts the

mass by about 8%, not bad!

Do the same problem with carbon dioxide (CO_2):

a) $P_R = \dfrac{P}{P_c} = \dfrac{150 \text{ bar}}{73.9 \text{ bar}} = 2.03$; $T_R = \dfrac{T}{T_c} = \dfrac{294 \text{ K}}{304 \text{ K}} = 0.97$

From the Generalized Compressibility Chart $Z \approx 0.3$

$v = 0.0011 \text{ m}^3\text{/kg} \rightarrow M = 38.2 \text{ kg}$

b) $M_{ideal} = 11.34 \text{ kg}$

Assuming the mass obtained from the chart is correct, the ideal gas model under predicts the mass by about 70%, bad!

Example:

A piston-cylinder assembly contains 1 kg of nitrogen gas (N_2). The gas expands from an initial state where $T_1 = 700K$ and $P_1 = 5$ bar to a final state where $P_2 = 2$ bar. During the process the pressure and specific volume are related by $Pv^{1.3} = const.$ *Assuming ideal gas* behaviour and neglecting KE and PE effects, determine the heat transfer during the process, in KJ.

$P_1 = 5$ bar $P_2 = 2$ bar
$T_1 = 700K$
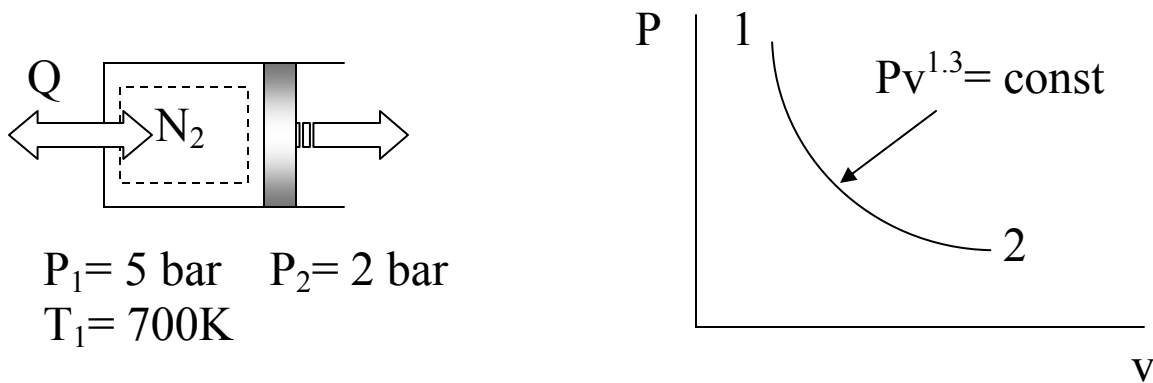
$$\Delta U = Q - W$$
$$Q = \Delta U + W$$

$$W = \int_1^2 pdV = \frac{P_2V_2 - P_1V_1}{1-n}$$

Recall, for an ideal gas $PV = MRT$

$$\int_1^2 pdV = \frac{MR(T_2 - T_1)}{1-n} \qquad \text{need } T_2$$

$$R = \frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2} \rightarrow \frac{P_1}{T_1}\left(\frac{const}{P_1^{1/n}}\right) = \frac{P_2}{T_2}\left(\frac{const}{P_2^{1/n}}\right)$$

$$\frac{P_1^{\frac{n-1}{n}}}{T_1} = \frac{P_2^{\frac{n-1}{n}}}{T_2} \rightarrow \boxed{\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}}} = \left(\frac{v_1^n}{v_2^n}\right)^{\frac{n-1}{n}} \rightarrow \boxed{\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{n-1}}$$

$$T_2 = \left(\frac{2\,\text{bar}}{5\,\text{bar}}\right)^{\frac{0.3}{1.3}}(700\text{K}) = 567\text{K}$$

$$W = \frac{MR(T_2 - T_1)}{1-n}$$
$$= \frac{1\,\text{kg}(8.314/28\,\text{kJ/kg}\cdot\text{K})(567 - 700)\text{K}}{1-1.3} = +\underline{132\text{kJ}}$$

Note: work is positive → work done by the system

The molar internal energy for nitrogen from Table A-23:

$$\bar{u}(700\text{K}) = 14{,}784\,\text{kJ/kmol}$$

$$\bar{u}(567\text{K}) = 11{,}858\,\text{kJ/kmol}$$

$$\Delta U = M(u_2 - u_1) = M\left(\frac{\bar{u}_2 - \bar{u}_1}{\mu}\right)$$

$$= 1\,\text{kg}\left(\frac{11{,}858 - 14{,}784 \text{ kJ/kmol}}{28 \text{ kg/kmol}}\right) = -\underline{104.5\,\text{kJ}}$$

Q= ΔU + W = (-104.5 kJ) + (132 kJ)= **+27.5 kJ**

Note: heat transfer is positive→ heat transferred into the system

Constant Specific Heat Assumption

This assumption can be made if the specific heat does not vary much in the temperature range of interest, use **average values** $\widetilde{c}_V$ and $\widetilde{c}_P$ such that:

$$u_2 - u_1 = \int_{T_1}^{T_2} c_V(T)dT = \widetilde{c}_V \int_{T_1}^{T_2} dT = \widetilde{c}_V(T_2 - T_1)$$

$$h_2 - h_1 = \int_{T_1}^{T_2} c_p(T)dT = \widetilde{c}_P \int_{T_1}^{T_2} dT = \widetilde{c}_P(T_2 - T_1)$$

the average value is taken to be

$$\widetilde{c}_V = \frac{c_V(T_1) + c_V(T_2)}{2} \qquad \widetilde{c}_P = \frac{c_P(T_1) + c_P(T_2)}{2}$$

Example:

Recalculate ΔU in last example assuming constant specific heat

The specific heats for nitrogen from Table A-20 for the two temperatures are

$$c_V(700\text{K}) = 0.801\,\text{kJ/kg} \cdot \text{K}$$

$$c_V(567\text{K}) = 0.771\,\text{kJ/kg} \cdot \text{K}$$

The average value over the temperature range is thus

$$\widetilde{c}_V = \frac{(0.801 + 0.771)}{2} = 0.786 \text{ kJ/kg} \cdot \text{K}$$

$$\Delta U = M(u_2 - u_1) = M\widetilde{c}_V(T_2 - T_1)$$
$$= 1 \text{ kg } (0.786 \text{kJ/kg} \cdot \text{K})(567 \text{ - } 700)\text{K}$$
$$= \text{-} \underline{104.5 \text{ kJ}}$$

The value for ΔU obtained using Table A-23 which takes into account the change in c_V with temperature is exactly the same!!

If tables are not available can approximate c_V by using the specific heat ratio K, which in the temperature range of 300K to 1000K, is taken to be constant (see Table A-20):

Diatomic molecules → K= 7/5= 1.4
(N_2, O_2, H_2, CO, "Air",…)

Monatomic molecules → K=5/3=1.67
(Ar, He, Ne,…)

$$c_V = \frac{R}{K-1} = \frac{8.314/28 \text{ kJ/kg} \cdot \text{K}}{1.4 \text{ - } 1} = \underline{0.742 \text{ kJ/kg} \cdot \text{K}}$$

compared to 0.786 kJ/kgK calculated above

Incompressible Assumption

A substance is **incompressible** if there is negligible change in specific volume with change in pressure, e.g., liquids and solids

The specific internal energy of an incompressible substance does not vary much with pressure, therefore the specific heat only depends on temperature

$$c_V(T) = \left.\frac{du(T)}{dT}\right|_{v\,\text{const}}$$

By definition enthalpy varies both with P and T

$$h(P,T) = u(T) + Pv$$

For incompressible v is constant, differentiating with respect to T while maintaining P constant yields,

$$\left.\frac{dh(T)}{dT}\right|_{P\,\text{const}} = \left.\frac{du(T)}{dT}\right|_{v\,\text{const}}$$

$$\boxed{c_P = c_v = c}$$

$$u_2 - u_1 = \int_1^2 c(T)dT$$

Also, $\Delta h = \Delta(u + Pv)$

$$h_2 - h_1 = (u_2 - u_1) + (P_2 v_2 - P_1 v_1)$$

$$h_2 - h_1 = \int_1^2 c(T)dT + v(P_2 - P_1)$$

Two special cases:

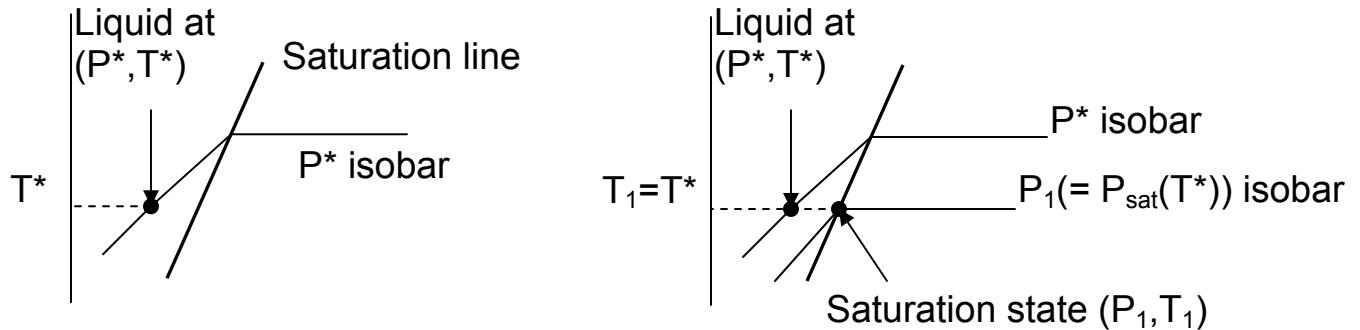i) Constant pressure heat addition into an incompressible substance (P= const.)

$$h_2 - h_1 = \int_1^2 c(T)dT$$

ii) Isothermal heat addition into an incompressible substance (T= const.)

$$h_2 - h_1 = v(P_2 - P_1)$$

Approximating enthalpy in the compressed liquid region of steam tables

Want to get enthalpy at (P*, T*) without using compressible liquid tables

Consider the isothermal process (incompressible) from $(P_1, T_1) \rightarrow (P*, T*)$ we now know $h* - h_1 = v(P* - P_1)$

$$h* = h_1 + v(P* - P_1)$$

$$\boxed{h(P*, T*) = h_{f\,sat}(T*) + v_{f\,sat}(T*)\left[(P* - P_{sat}(T*))\right]}$$

This gives a more accurate result than just taking $h(P*, T*) = h_{f\,sat}(T*)$ as proposed earlier for $u(P*, T*)$

The last term is a correction which is normally small because v_{fsat} is very small