④ APPLICATIONS OF THE FIRST LAW (GENERAL)

1] HEAT CAPACITY

THIS MEASURES THE HEAT, δQ, REQUIRED TO RAISE THE TEMPERATURE BY dT:

$$C \equiv \frac{\delta Q}{dT} \tag{1}$$

ACTUALLY, THIS IS SOMEWHAT AMBIGUOUS, ESPECIALLY FOR GASES. TO RAISE AIR BY 1°C REQUIRES MORE ENERGY IF ALLOWED TO EXPAND THAN IF HELD AT CONSTANT VOLUME. AND SO WE SEPARATELY DEFINE:

$$C_V \equiv \Big(\frac{\delta Q}{dT}\Big)_{\underset{V\text{ - CONSTANT}}{\uparrow}\!V} \quad \& \quad C_P \equiv \Big(\frac{\delta Q}{dT}\Big)_{\underset{P\text{ - CONSTANT.}}{\uparrow}\!P}, \tag{2}$$

THE HEAT CAPACITIES AT CONSTANT VOLUME AND PRESSURE, RESPECTIVELY.

THESE ARE EXTENSIVE PROPERTIES. INTENSIVE PROPERTIES ARE FOUND BY DIVIDING BY MASS TO GIVE THE "SPECIFIC HEATS":

$$c_V \equiv \frac{1}{n}\Big(\frac{\delta Q}{dT}\Big)_V \equiv \Big(\frac{\delta q}{dT}\Big)_V \quad \& \quad c_P \equiv \frac{1}{n}\Big(\frac{\delta Q}{dT}\Big)_P \equiv \Big(\frac{\delta q}{dT}\Big)_P$$

[THIS IS THE TEXT'S DEFINITION, GIVING c_V & c_P IN UNITS OF J/(mol K). MORE STANDARD IS TO ACTUALLY DIVIDE BY MASS, KNOWING THE MOLAR MASS OF THE SUBSTANCE]

FROM THE FIRST LAW, $dU = \delta Q - PdV$, IT FOLLOWS THAT FOR A SYSTEM AT CONSTANT VOLUME $\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\delta Q}{dT}\right)_V = C_V$

$$\boxed{dU = C_V\, dT} \tag{3}$$

FOR AN IDEAL GAS C_V AND C_P ARE DIRECTLY RELATED.

FROM $PV = nRT \Rightarrow VdP + PdV = nR\,dT \Rightarrow PdV = -VdP + nR\,dT$

SO FROM FIRST LAW, USING ③ $\Rightarrow C_V\,dT = \delta Q + VdP - nR\,dT$

NOW CONSIDER AN ISOBARIC SYSTEM $\Rightarrow \delta Q = C_P\,dT$ & $VdP = 0$

SO $$C_V\,dT = C_P\,dT - nR\,dT$$

$$\Rightarrow \quad C_P = C_V + nR$$

IN TERMS OF SPECIFIC HEATS: $$\boxed{c_P = c_V + R} \tag{4}$$

EXAMPLE: FOR AIR $c_V = 718$ J/(kg·K), $R_a = 287$ J/(kg K) $\Rightarrow c_P = 1005$ J/(kg·K)

2] ENTHALPY

WHEREAS THE INTERNAL ENERGY, U, IS USEFUL FOR SYSTEMS KEPT AT CONSTANT VOLUME $(dU = \delta Q - PdV = \delta Q)$, ENTHALPY IS USEFUL FOR SYSTEMS KEPT AT CONSTANT PRESSURE. EXPLICITLY, DEFINE <u>ENTHALPY</u> AS

$$H \equiv U + PV. \qquad ①$$

THEN, IN AN ISOBARIC SYSTEM $dH = dU + d(PV) = dU + PdV + VdP$.

SO, WITH $dP = 0 \Rightarrow \quad dH = dU + PdV$. ②

COMBINED WITH FIRST LAW, $dU = \delta Q - PdV - \delta W_{OTHER}$

$$\Rightarrow \boxed{dH = \delta Q - \delta W_{OTHER},} \qquad P\text{-CONSTANT} \qquad ③$$

IN WHICH δW_{OTHER} IS NON-COMPRESSIONAL WORK (eg FROM MICROWAVES, ELECTRICITY, etc).

IN THE ABSENCE OF OTHER WORK, ENTHALPY CHANGES ONLY AS A RESULT OF HEAT INPUT FOR A SYSTEM AT CONSTANT PRESSURE. SO HEAT CAPACITY AT CONSTANT PRESSURE IS

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad ④$$

$$\text{SO} \quad dH = C_p\, dT$$

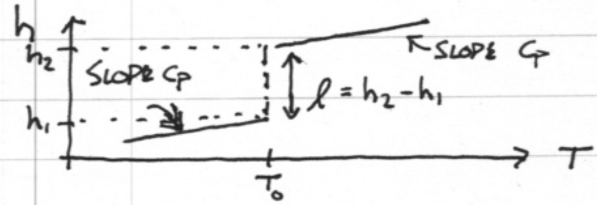
EVEN IF NOT AT CONSTANT PRESSURE, THE FIRST LAW CAN BE REWRITTEN IN TERMS OF ENTHALPY. IGNORING OTHER WORK WE HAVE $C_p dT = dH = \delta Q + VdP$ ⑤

OR $\quad c_p dT = dh = \delta q + \frac{1}{\rho}\, dP \quad$ (SPECIFIC ENTHALPY)

H (AND h) IS A STATE VARIABLE AND dH (AND dh) IS A TOTAL DIFFERENTIAL $\quad \oint dH = 0$

3] HEATS OF TRANSFORMATION

ONE OF THE MOST COMMON APPLICATIONS OF ENTHALPY IS IN CHARACTERIZING THE CHANGE OF PHASE BETWEEN SOLID, LIQUID AND GAS. Eg. AS AN ICE CUBE FIRST MELTS AND THEN EVAPORATES, THE VOLUME OCCUPIED BY THE WATER MOLECULES CHANGES SUBSTANTIALLY, BUT THE PROCESSES ALL TAKE PLACE AT THE SAME PRESSURE. FURTHERMORE THE TEMPERATURE IS CONSTANT DURING THE TRANSFORMATION.



PLOT SHOWING SPECIFIC ENTHALPY OF A SUBSTANCE AS IT CHANGES PHASE ABOUT TEMPERATURE T_0

THE "<u>LATENT HEAT</u>" MEASURES THE CHANGE IN SPECIFIC ENTHALPY DURING A CHANGE IN PHASE: $\ell = \delta Q/M = \delta q$ IS THE HEAT δQ REQUIRED TO CHANGE THE PHASE PER MASS M OF SUBSTANCE. SPECIFICALLY ℓ_f IS THE "LATENT HEAT OF FUSION" (FOR MELTING) AND ℓ_v IS THE "LATENT HEAT OF VAPOORIZATION" (FOR EVAPORATION)

SOME VALUES: WATER: $\ell_f = 3.33 \times 10^5$ J/kg , $\ell_v = 2.25 \times 10^6$ J/kg
MERCURY: $\ell_f = 1.26 \times 10^4$ J/kg , $\ell_v = 2.64 \times 10^5$ J/kg
ETHYL ALCOHOL: $\ell_v = 8.66 \times 10^5$ J/kg

AMAZING FACTS ABOUT WATER:

c_v ($\approx 4.2 \times 10^3$ J/(kg K) IS LARGEST OF <u>ALL</u> LIQUIDS

$\Rightarrow$ LARGE HEAT STORAGE IN OCEANS

ℓ_v IS LARGEST OF <u>ALL</u> LIQUIDS

$\Rightarrow$ LARGE HEAT TRANSPORT BY DROPS $\Leftrightarrow$ VAPOR IN CLOUDS

... AND MANY OTHER RECORD BREAKERS BESIDES (LARGEST DIELECTRIC CONSTANT $\Rightarrow$ GREAT SOLVENT; LARGEST SURFACE TENSION NEXT TO MERCURY $\Rightarrow$ BIG RAIN DROPS)

4] ADIABATIC COMPRESSION OF AN IDEAL GAS

IN AN "ADIABATIC" PROCESS, HEAT DOES NOT ENTER OR LEAVE THE SYSTEM. Eg IT IS INSULATED OR THE PROCESS IS SO FAST THE HEAT HAS NO TIME TO ESCAPE VIA RADIATION OF IR LIGHT.

FROM FIRST LAW (eg EQ^{N} ② ON p.20 OF NOTES) USING $dU = C_V dT$ AND ASSUMING ADIABATIC ($\delta Q = 0$), WE HAVE

$$C_V\, dT = -P\, dV \qquad ①$$

IN WHICH C_V IS ASSUMED CONSTANT (A RESULT FROM STATISTICAL MECHANICS ... WAIT FOR IT) AND $P = \frac{1}{V}(nRT)$ (FROM EQUATION OF STATE). SO ① BECOMES

$$C_V\, dT = -\frac{1}{V}(nRT)\, dV \Rightarrow \frac{C_V}{nR}\frac{1}{T}dT = -\frac{1}{V}dV \qquad ②$$

INTEGRATE BOTH SIDES

$$\Rightarrow \frac{C_V}{nR}\ln T = -\ln V + \overset{\text{CONSTANT}}{\mathcal{C}}$$

$$\Rightarrow T^{(C_V/nR)} = \mathcal{C}'\frac{1}{V}$$

$$\Rightarrow V T^{(C_V/nR)} = \mathcal{C}' = \overset{\text{INITIAL VALUES BEFORE COMPRESSION}}{V_0 T_0}{}^{(C_V/nR)} \qquad ③$$

RECALL $C_P = C_V + nR \Rightarrow \frac{C_V}{nR} = \frac{C_V}{C_P - C_V} = \frac{1}{(C_P/C_V) - 1}$

DEFINE $\boxed{\gamma \equiv \frac{C_P}{C_V}}$, THE "ADIABATIC CONSTANT" ④

[FROM STATISTICAL MECHANICS WE WILL SEE THAT $\gamma \simeq 5/3$ FOR A MONATOMIC GAS (He, Ar, ..) AND $\gamma \simeq 7/5$ FOR A DIATOMIC GAS (O_2, N_2, ~AIR, ...)]

SO ③ IS WRITTEN $V T^{\frac{1}{\gamma-1}} = V_0 T_0^{\frac{1}{\gamma-1}}$ OR, MORE EXPLICITLY:

$$\boxed{T = T_0 (V/V_0)^{1-\gamma}} \qquad ⑤$$

EXAMPLE: 1L OF AIR IN A BICYCLE PUMP AT 20°C IS RAPIDLY COMPRESSED BY 10%. WHAT IS ITS TEMPERATURE?

SOL^{N}: $T \simeq (273 + 20)(0.9/1)^{1-(7/5)} = 293(0.9)^{-2/5}$

$$\simeq 306\,K \simeq 33°C \;//$$

4] (CONT'D)

GIVEN EQUATION ⑤, WE CAN USE THE EQUATION OF STATE TO RELATE TEMPERATURE TO PRESSURE AND PRESSURE TO VOLUME (OR DENSITY) IN AN ADIABATIC PROCESS.

$$T = T_0\left[(nRT/P)/(nRT_0/P_0)\right]^{1-\gamma} = T_0\left(\frac{T}{T_0}\right)^{1-\gamma}\left(\frac{P}{P_0}\right)^{\gamma-1}$$

$$\Rightarrow \left(\frac{T}{T_0}\right)^{\gamma} = \left(\frac{P}{P_0}\right)^{\gamma-1}$$

$$\Rightarrow \boxed{T = T_0\,(P/P_0)^{\varkappa}} \quad \text{WITH } \varkappa \equiv 1-\frac{1}{\gamma} \qquad ⑥$$

($\varkappa \simeq 2/5$ FOR A MONATOMIC GAS ; $\varkappa \simeq 2/7$ FOR A DIATOMIC GAS)

EXAMPLE: DRY AIR AT THE GROUND (PRESSURE 1 BAR = 1000 mBAR) WITH TEMPERATURE 20°C MOVES ADIABATICALLY UPWARDS TO THE TOP OF THE TROPOSPHERE WHERE THE PRESSURE IS 250 mBAR. WHAT IS ITS TEMPERATURE?

SOL^N:

$$T \simeq (273+20)(250/1000)^{2/7}$$

$$\simeq 197\,\text{K} \simeq -76\,\text{K} \; //$$

LIKEWISE RELATING PRESSURE TO VOLUME AND DENSITY GIVES:

$$\boxed{\begin{aligned} P &= P_0\,(V/V_0)^{-\gamma} \\ P &= P_0\,(\rho/\rho_0)^{\gamma} \end{aligned}} \qquad \begin{aligned} ⑦ \\ ⑧ \end{aligned}$$

EQUATION ⑦ ALLOWS US TO COMPUTE THE "PdV WORK" OF AN ADIABATIC PROCESS (SEE p. 18 OF NOTES)

$$W = \int_{V_i}^{V_f} P\,dV = \int_{V_i}^{V_f} P_i\,(V/V_i)^{-\gamma}\,dV$$

$$= P_i V_i \,\frac{1}{1-\gamma}\,(V/V_i)^{1-\gamma}\Big|_{V_i}^{V_f}$$

$$= \frac{1}{1-\gamma}\,P_i V_i\left[(V_f/V_i)^{1-\gamma} - 1\right] \qquad ⑨$$

$$= \frac{1}{1-\gamma}\left[P_i V_f\,(V_f/V_i)^{-\gamma} - P_i V_i\right] = \frac{1}{1-\gamma}\left[P_f V_f - P_i V_i\right]$$

EXAMPLE: COMPRESS 10 L OF AIR AT 1 BAR ADIABATICALLY TO 9 L.

$$\Rightarrow P_f \simeq (10^5\,\text{Pa})(9/10)^{-7/5} \simeq 1.16\times10^5\,\text{Pa}$$

$$\Rightarrow W \simeq \frac{1}{1-7/5}\left[(1.16\times10^5\,\text{Pa})(9\times10^{-3}\,\text{m}^3) - (10^5\,\text{Pa})(10\times10^{-3}\,\text{m}^3)\right]$$

$$\simeq -108\,\text{J} \; //$$

[COMPARE w. −107 J FOR ISOTHERMAL COMPRESSION]