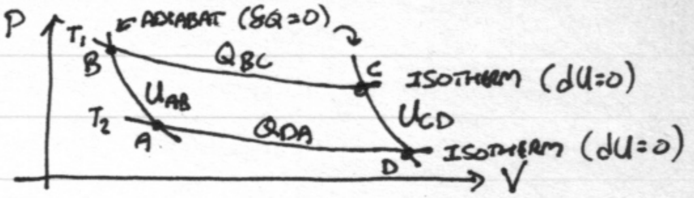
⑥ THE SECOND LAW OF THERMODYNAMICS

1] THERMODYNAMIC DEFINITION OF ENTROPY

RECALL OUR CONSIDERATION OF ENERGY AT EACH STEP IN THE CARNOT HEAT ENGINE

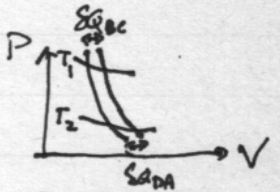


CONSISTENT WITH $dU = 0$ ALONG ISOTHERMS FOUND $U_{CD} = -U_{AB}$

ALONG $\overline{BC}$ AND $\overline{DA}$ FOUND THAT HEATS WERE RELATED BY

$$\frac{1}{T_2} Q_{DA} = -\frac{1}{T_1} Q_{BC} \qquad (*)$$

WE ARRIVED AT THIS EXPRESSION ALL THE HEAT WENT INTO AND CAME OUT OF PdV WORK. I.e. NO ADDITIONAL LOSSES DUE TO RADIATION, HEAT DIFFUSION, etc. I.e. A REVERSIBLE PROCESS.



NOW SUPPOSE THE HEATS IN AND OUT ARE VERY SMALL

SO WE CAN WRITE $Q_{DA} \to \delta Q_{DA}$, $Q_{BC} \to \delta Q_{BC}$ AS INFINITESIMALS

THE RESULT (*) INSPIRES US TO DEFINE A DIFFERENTIAL

$$\boxed{dS \equiv \frac{1}{T} \delta Q}$$

THIS IS THE CLAPEYRON DEFINITION OF ENTROPY, S. (1843)

[IT WORKS FOR ALL SUBSTANCES, NOT JUST AN IDEAL GAS]

NOTE, IN GOING AROUND THE CARNOT CYCLE

$$\begin{aligned}\oint dS &= \int_A^B \frac{1}{T}\delta Q + \int_B^C \frac{1}{T_1}\delta Q + \int_C^D \frac{1}{T}\delta Q + \int_D^A \frac{1}{T_2}\delta Q \\ &= 0 + \frac{1}{T_1} Q_{BC} + 0 + \frac{1}{T_2} Q_{DA} \\ &= 0 \qquad (\text{USING } (*))\end{aligned}$$

SO, IN A REVERSIBLE PROCESS $\oint dS = 0$

$\Rightarrow$ S IS INDEPENDENT OF PATH

$\Rightarrow$ S IS A STATE VARIABLE, LIKE U, P, T, V etc

2] THE SECOND LAW OF THERMODYNAMICS

IN IRREVERSIBLE PROCESSES SOME ENERGY FROM WORK (eg PdV) IS LOST (e.g. THROUGH FRICTION) BEING TRANSFORMED INTO RADIATED OR CONDUCTED HEAT ENERGY THAT CAN NEVER BE RETURNED AS WORK. [LIKEWISE, A BATTERY CAN PASS A CURRENT THROUGH A RESISTOR HEATING IT UP, BUT HEATING A RESISTOR WILL NOT CHARGE A BATTERY].

SO WE CAN WRITE $$\underbrace{\overbrace{\delta W}^{\text{TOTAL WORK}} = \overbrace{\delta W_r}^{\text{REVERSIBLE WORK (e.g. PdV)}} - \overset{\swarrow\ \text{DISSIPATIVE WORK}}{\varepsilon}}_{\text{OF SYSTEM ON ENVIRONMENT}} , \quad \varepsilon > 0$$

BY ENERGY CONSERVATION, THE DISSIPATIVE WORK BECOMES HEAT WHICH IS NOT PART OF A REVERSIBLE PROCESS

SO WE CAN WRITE $$\overbrace{\delta Q}^{\text{TOTAL HEAT OF SYSTEM}} = \overbrace{\delta Q_r}^{\text{HEAT FROM REVERSIBLE WORK}} - \overbrace{\varepsilon}^{\rightarrow \text{HEAT LOST BY DISSIPATION}}$$

NOTE, THE INTERNAL ENERGY DOESN'T CHANGE WHETHER REVERSIBLE OR NOT

$$dU = \delta Q - \delta W = (\delta Q_r - \varepsilon) - (\delta W_r - \varepsilon) = \delta Q_r - \delta W_r$$

IMPORTANTLY, $\varepsilon > 0$ SO $\delta Q_r \geq \delta Q$ WITH EQUALITY ONLY FOR REVERSIBLE PROCESSES.

RECASTING THIS IN TERMS OF ENTROPY, WHICH NOW IS DEFINED EXPLICITLY FOR HEAT ASSOCIATED WITH REVERSIBLE PROCESSES:

$$\Rightarrow \quad dS = \frac{\delta Q_r}{T} \geq \frac{\delta Q}{T} \geq 0$$

SO $dS \geq 0$ WITH EQUALITY FOR ADIABATIC PROCESSES ($\delta Q = 0$)

THIS IS <u>2</u>

THIS IS 2^{ND} LAW OF THERMODYNAMICS: ENTROPY ALWAYS INCREASES OR, AT BEST, IS CONSTANT.

3] FIRST LAW OF THERMODYNAMICS (REPRISE)

BEFORE WE HAD $dU = \delta Q - P\,dV$

NOW, WITH $dS \equiv \frac{\delta Q}{T}$ WE CAN WRITE THE 1ST LAW IN TERMS OF DIFFERENTIALS IN EACH TERM:

$$\boxed{dU = T\,dS - P\,dV}$$

THUS WE THINK OF $U \equiv U(S,V)$, AND IT IS UNDERSTOOD THAT $T = T(S,V)$, $P(S,V)$ IN GENERAL.

COMPARE WITH TOTAL DIFFERENTIAL OF U: $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$

SO (<u>AT LAST</u>) WE HAVE AN EXPLICIT (THOUGH NOT INTUITIVE) DEFINITION OF TEMPERATURE:

$$T = \left(\frac{\partial U}{\partial S}\right)_V$$

ALSO

$$P = -\left(\frac{\partial U}{\partial V}\right)_S$$

ALTERNATELY, WE CAN WRITE 1ST LAW IN TERMS OF ENTHALPY:

$$\boxed{dH = T\,dS + V\,dP}$$

IN WHICH WE UNDERSTAND $H \equiv H(S,P)$

AGAIN COMPARED WITH $dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$

$$\Rightarrow T = \left(\frac{\partial H}{\partial S}\right)_P \;;\; V = \left(\frac{\partial H}{\partial P}\right)_S$$

THESE FORMULAE CAN ALSO BE WRITTEN IN INTRINSIC PROPERTIES

$$du = T\,ds - P\,dv$$
$$dh = T\,ds + v\,dP$$

$s = \frac{1}{n} S$ (OR $\frac{1}{M} S$) IS THE "SPECIFIC ENTROPY"

4] GIBBS + HELMHOLTZ FREE ENERGIES

$U^{(S,V)}$ (INTERNAL ENERGY) AND $H^{(S,P)}$ (ENTHALPY) ARE TWO OF FOUR COMMONLY USED ENERGIES IN THERMODYNAMICS. THE OTHER TWO REPLACE S WITH T AS THE STATE VARIABLE.

HELMHOLTZ FREE ENERGY: $F \equiv U - TS$, $F = F(T,V)$

$$\Rightarrow \quad dF = dU - TdS - SdT \overset{1^{ST}\text{ LAW}}{=} \underline{-SdT - PdV}$$

GIBBS FREE ENERGY: $G \equiv U - TS + PV = H - TS$, $G = G(T,P)$

$$\Rightarrow \quad \boxed{dG = -SdT + VdP}$$

WE WILL SEE THAT GIBBS FREE ENERGY IS PARTICULARLY USEFUL TO STUDY PHASE TRANSFORMATIONS (FOR WHICH T AND P ARE CONSTANTS).

THE GIBBS FREE ENERGY IS ALSO USED (AS OF 2010) TO CHARACTERIZE THE THERMODYNAMIC PROPERTIES OF SEA WATER. THIS IS BECAUSE THE ARGUMENTS TO G ARE DIRECTLY MEASUREABLE.

THE FOUR QUANTITIES U, H, F AND G ARE CALLED "<u>THERMODYNAMIC POTENTIALS</u>"

THE EXPRESSIONS OF THE 1ST LAW FOR dU, dH, dF, dG ARE CALLED "THERMODYNAMIC IDENTITIES"

5] MAXWELL RELATIONS

WE FOUND $dU = TdS - PdV \Rightarrow T = \left(\frac{\partial U}{\partial S}\right)$, $P = -\left(\frac{\partial U}{\partial V}\right)$

ASSUMING $U(S,V)$ IS "NICE" (AKA TWICE DEFFERENTIABLE etc)

WE KNOW $\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$ (ORDER OF DERIVATIVES DOESN'T MATTER)

AND SO WE HAVE $\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$

THIS IS ONE OF MAXWELL'S RELATIONS. ANOTHER RELATION IS FOUND FROM ENTHALPY:

$$dH = TdS + VdP \Rightarrow T = \left(\frac{\partial H}{\partial S}\right)_P , \; V = \left(\frac{\partial H}{\partial P}\right)_S$$

$$\Rightarrow \boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P}$$

FROM ~~H~~ELMHOLTZ FREE ENERGY:

$$dF = -SdT - PdV \Rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_V , \; P = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}$$

FROM GIBBS FREE ENERGY:

$$dG = -SdT + VdP \Rightarrow S = -\left(\frac{\partial G}{\partial T}\right)_P , \; V = +\left(\frac{\partial G}{\partial P}\right)_T$$

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P}$$

6] RECIPROCAL RELATIONS & CYCLICAL RELATIONS

IN WHAT FOLLOWS WE WILL NEED SOME USEFUL IDENTITIES INVOLVING 3 PROPERTIES x, y, z (e.g. P, V & T) INTERRELATED BY SOME FORMULA EXPRESSED ABSTRACTLY AS $f(x,y,z) = 0$.

WRITTEN EXPLICITLY AS $x = x(y,z)$, WE GET THE DIFFERENTIAL

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \qquad \textcircled{1}$$

WRITTEN EXPLICITLY AS $y = y(x,z)$, WE GET THE DIFFERENTIAL

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \qquad \textcircled{2}$$

SUBSTITUTING ② INTO ① GIVES

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz \qquad \textcircled{3}$$

IF x & z ARE CONSIDERED AS THE INDEPENDENT VARIABLES, THEN ③ HOLDS FOR ALL dx & dz.

IN PARTICULAR, IF $dz = 0$ AND $dx \neq 0$, ③ $\Rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1$

$$\Rightarrow \boxed{\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}}$$

THE "<u>RECIPROCAL RELATION</u>" ④

IF $dx = 0$ AND $dz \neq 0$, ③ $\Rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y$ ⑤

SOMETIMES ⑤ IS REWRITTEN USING THE RECIPROCAL RELATION $\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{(\partial z/\partial x)_y}$

$$\Rightarrow \boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1}$$

THE "<u>CYCLICAL RELATION</u>" ⑥

THE NEGATIVE SIGN IS A RESULT OF CHANGING SUBSCRIPTS IN ⑥.

DO NOT CONFUSE ⑤ WITH THE CHAIN RULE OF DIFFERENTIATION!

$$\left(\frac{\partial x}{\partial z}\right)_u = \left(\frac{\partial x}{\partial y}\right)_u \left(\frac{\partial y}{\partial z}\right)_u \quad \leftarrow \text{NO NEGATIVE SIGN}$$

IN WHICH $u \equiv u(x,y)$ FIXED IMPLICITLY RELATES x & y