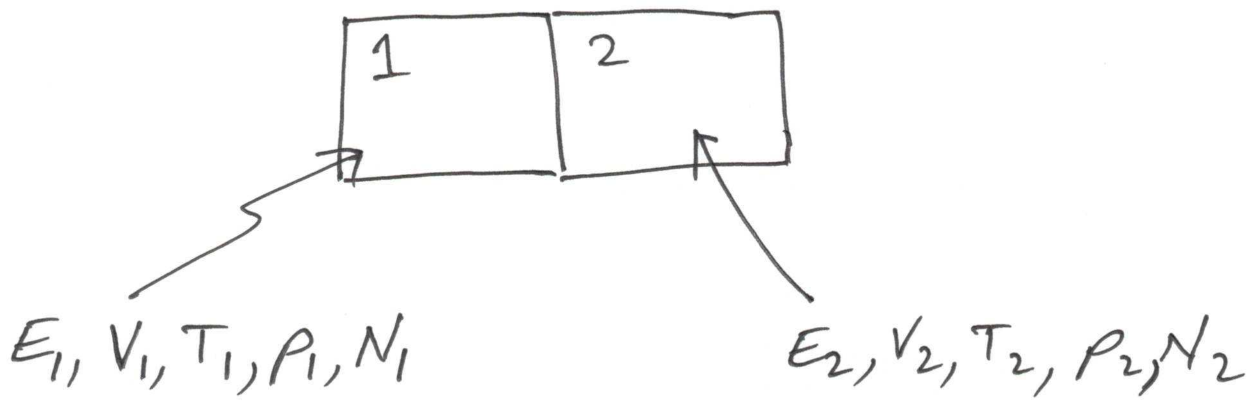
EXTENSIVE & INTENSIVE PARAMETERS

EXAMPLE: CONSIDER A SYSTEM CONSISTING OF TWO SUBSYSTEMS 1 & 2.



FOR THE TOTAL SYSTEM = SUBSYSTEM 1 + SUBSYSTEM 2

NOTICE THAT IN GENERAL

$$\left.\begin{aligned} E_{TOTAL} &= E_1 + E_2 \\ V_{TOTAL} &= V_1 + V_2 \\ N_{TOTAL} &= N_1 + N_2 \end{aligned}\right\} \text{EXAMPLES OF } \underline{\text{EXTENSIVE}} \text{ PARAMETERS}$$

BUT IN GENERAL

$$\left.\begin{array}{l} P_{TOTAL} \neq P_1 + P_2 \\ \\ T_{TOTAL} \neq T_1 + T_2 \end{array}\right\} \text{EXAMPLES OF } \underline{\text{INTENSIVE}} \text{ PARAMETERS}$$

<u>MOLAR SPECIFIC HEATS</u> (MSH)

DEFINE

C_V = MSH AT CONST VOLUME

C_P = MSH AT CONST PRESSURE

$$C_P \neq C_V$$

WHY?

RECALL

$$\boxed{đQ = dE + p\,dV}$$

1ST LAW QUASISTATIC PROCESS.

AT CONST V $\quad dV = 0 \quad \Rightarrow \quad \boxed{đQ = dE}$

AT CONST p $\quad dV > 0$ SO SOME OF THE $đQ$ GOES INTO BOTH E & WORK

$\Rightarrow C_p > C_V$ [MORE ENERGY REQUIRED FOR CONST p TO GET THE SAME TEMP RISE SINCE THE SYSTEM WILL DO WORK ON SURROUNDINGS.]

FOR IDEAL GAS:

$$E = \alpha N k_B T = \alpha \nu R T$$

$$\Rightarrow dE = \alpha k_B \, dN \, T + \alpha k_B N \, dT$$

IF $N = \text{CONST}$

$$dE = \alpha k_B N \, dT = \alpha \nu R \, dT$$

$$\Rightarrow \boxed{đQ = \alpha \nu R \, dT + p \, dV} \quad (1)$$

FOR CONST V $\quad dV = 0$

$\Rightarrow$ (1) BECOMES $\quad đQ = \alpha \nu R \, dT$

$$\Rightarrow \boxed{C_V = \frac{1}{\nu} \frac{đQ}{dT} = \alpha R} \quad (2)$$

THUS $\quad \boxed{E = \nu C_V T} \quad (3)$

FOR CONST p : $dp = 0$

So (1) BECOMES

$$đQ = \alpha \nu R dT + p dV$$

$$= \nu C_V dT + p dV \quad \text{BY (2)}$$

$$= \nu C_V dT + d(pV)$$

[SINCE $d(pV) = dp\, V + p dV$
$= p dV$ IF $dp = 0$]

$pV = \nu R T$

$$\Longrightarrow \quad đQ = \nu C_V dT + d(\nu R T)$$

$$= \nu C_V dT + \nu R dT$$

$$\Longrightarrow \quad \boxed{đQ = \nu (C_V + R) dT}$$

THUS

$$\boxed{C_p = \frac{1}{\nu}\frac{đQ}{dT} = C_V + R}$$

FOR IDEAL GASES $\boxed{C_p = C_V + R}$

ENTROPY OF AN IDEAL GAS

1ST LAW : $đQ = dE - đW$

QUASISTATIC : $đQ = dE + p\,dV$

FOR ν MOLES OF AN IDEAL GAS

$$E = \nu C_V T \implies dE = \nu C_V\,dT$$

SO

$$\boxed{đQ = \nu C_V\,dT + p\,dV}$$

USING THE EQUATION OF STATE

$$pV = \nu RT$$

WE FIND

$$đQ = \nu C_V dT + \frac{\nu RT}{V} dV$$

$$\Rightarrow \frac{đQ}{T} = \nu C_V \frac{dT}{T} + \nu R \frac{dV}{V}$$

$$\Rightarrow \frac{đQ}{T} = \nu C_V d(\ln T) + \nu R d(\ln V)$$

ASIDE FOR A FUNCTION OF A SINGLE VARIABLE $f(x)$

$$df(x) = \frac{\partial f}{\partial x} dx \Longrightarrow d(\ln x) = \frac{1}{x} dx$$

SO $$\boxed{\frac{đQ}{T} = d\underbrace{\left(\nu C_V \ln T + \nu R \ln V + \text{CONST}\right)}_{\text{EXACT DIFFERENTIAL}}}$$

NOTICE THAT ALTHOUGH $đQ$ IS AN INEXACT DIFFERENTIAL, THE RIGHT-HAND-SIDE OF THE LAST EXPRESSION IS AN EXACT DIFFERENTIAL, SO

$$\frac{đQ}{T} \text{ — EXACT DIFFERENTIAL}$$

DEFINE A FUNCTION S SUCH THAT

$$\frac{đQ}{T} = dS$$

S = ENTROPY

SO FOR AN IDEAL GAS WE HAVE:

$$\boxed{S = \nu C_V \ln T + \nu R \ln V + \text{CONST}}$$

WE WILL USE STAT MECH TO DETERMINE THIS CONST LATER