LECTURE 4 1/27/11

RECAP

1) WE DEFINED "ABSOLUTE" TEMPERATURE

2) WE DERIVED AND DISCUSSED AN ENERGY CONSERVATION EQUATION

ACCUMULATION FLOW IN

$$\frac{d}{dt}\left[m\left(U + \frac{u^2}{2g_c} + \frac{gz}{g_c}\right)\right] = \sum_{\text{INLETS}} \dot{m}^{in}\left(H + \frac{u^2}{2g_c} + \frac{gz}{g_c}\right)$$

FLOW OUT

DIFFERENT!!

$$- \sum_{\text{OUTLETS}} \dot{m}^{out}\left(H + \frac{u^2}{2g_c} + \frac{gz}{g_c}\right)$$

$$+ \sum \underline{\dot{Q}} + \underline{\dot{W}_s}$$

HEAT IN/OUT

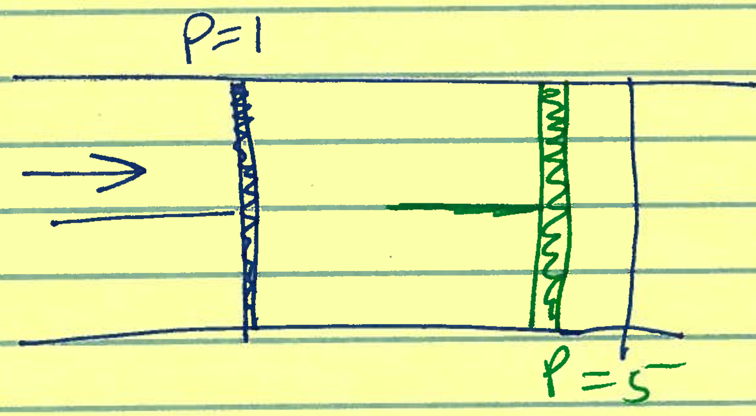
ROTATING SHAFT WORK

$$- p\frac{d\underline{V}}{dt}$$

"P-V" WORK CAUSED BY CHANGE IN SIZE OF CONTAINER

3 WE USED THE ENERGY BALANCE TO ANALYZE A PISTON/CYLINDER TO COMPRESS AN IDEAL GAS

$P = 1$ ATM → 5 ATM



$$d\underline{U} = d\underline{Q} - P\,d\underline{V}$$

$$\underline{W}_{EC} = -\int P\,d\underline{V}$$

$$\boxed{\underline{W}_{EC} = RT \ln \frac{P_2}{P_1}}$$

$$W_{EC} = (8.314)(298)\ln 5 = 3990 \frac{J}{MOLE}$$

$$\underline{W}_{EC} \sim T$$

↑ ABSOLUTE TEMP

(MAKES SENSE ONLY W/ ABSOLUTE T)

BACK TO ENERGY BALANCE

$$dU = dQ - PdV$$

WHAT ABOUT THE OTHER TERMS?

WE COULD SURMISE THAT SOME Q WENT IN OR OUT (WHICH IS IT?) HOW MUCH?

ALSO, IS $\Delta U = 0$ OR SOME VALUE?

~~WE NEED TO FIGURE THIS OUT~~

~~WHAT ABOUT ΔU,? DID IT CHANGE?~~

SEEMS LIKE WE NEED SOME MORE TOOLS !!

$$\Delta U = Q - \underbrace{\int P\,dV}_{\text{WE KNOW THIS}}$$

THIS WILL LEAD TO A NEW GENERAL CONSTITUTIVE RELATION

SUPPOSE I DO AN EXPERIMENT WHERE A FIXED V CONTAINER CONTAINS A GAS.

SOME SMALL AMOUNT OF HEAT IS ADDED...

1) WHAT IS VALUE OF WORK?

SINCE $dW_{EC} = 0$

$$dU = dQ$$

$$dU = dQ$$

IF HEAT GOES IN, WE EXPECT THAT T WILL INCREASE.

$$Q = U_f - U_I = C(T_f - T_I)$$

$$C = \frac{U_f - U_I}{T_f - T_I}$$

IF THE Q IS VERY SMALL

DEFINITION OF A NEW GENERAL PROPERTY

$$C_V \equiv \left.\frac{\partial U}{\partial T}\right|_V$$

"HEAT CAPACITY" AT CONSTANT VOLUME

HOWEVER GENERALLY WE WILL TABULATE C_P

WE WILL BE ABLE TO TABULATE VALUES FOR C_V, FOR DIFFERENT GASES ~~#~~

AND USE THESE AS WE NEED THEM.

NOTE THAT IN GENERAL

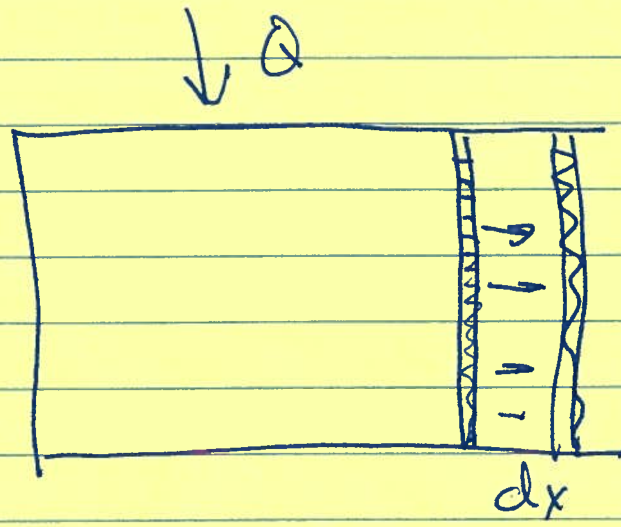
$$C_V = C_V(T, \cancel{P}V)$$

BUT OFTEN $C_V = C_V(T)$

AND, FOR A <u>REAL</u> IDEAL GAS $C_V = \underline{\underline{CONST}}$

WITH MORE EXAMPLES THE CONFUSION WILL BE LESS

WHILE WE ARE AT IT, LET'S DO THE SAME EXPERIMENT AT ~~CONST~~ CONSTANT P.



$P = \text{CONST}$

V INCREASES

$$dU = dQ - PdV$$

$$C(T_f - T_I) = Q = \Delta U - P\Delta V$$

$$= U_f - U_I - P(V_f - V_I)$$

$$C(T_f - T_I) = H_f - H_I$$

$$C_P \equiv \left.\frac{\partial H}{\partial T}\right|_P$$

HEAT CAPACITY AT CONST PRESSURE

AGAIN, AS WITH "H", IT IS EASIER TO MEASURE THAN C_V.

SO THIS IS WHAT WE TABULATE

$$C_P = C_P(T, P)$$

EXTENSIVE TABLES OF

C_P FOR MANY DIFFERENT

GASES ON PP 627 - - -

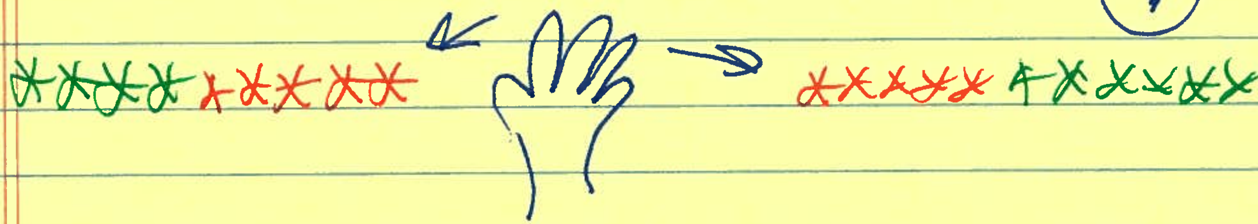
SO, NOW LETS GO BACK TO

OUR PROBLEM.

WE COMPRESSED AN IDEAL

GAS, CAN WE SAY

ANYTHING ABOUT dU OR dQ?



BECAUSE AN IDEAL GAS DOES NOT HAVE ANY ATTRACTION/ REPULSION BETWEEN ATOMS/ MOLECUES AND BECAUSE COLLISIONS ARE INFREQUENT

THE INTERNAL ENERGY ~~OF~~ DEPENDS ONLY ON THE AVERAGE KINETIC ENERGY OF THE MOLECULES

HENCE

$$U = U(T)$$

IDEAL GAS

$$dU = C_v\, dT$$

$$\Delta U = C_v \Delta T \quad \text{IF } C_v = \text{CONST}$$

FOR A REAL GAS ONLY IF V=CONST

$$= \int_{T_1}^{T_2} C_v\, dT$$

SIMILARLY

$$\Delta H = \int_{T_1}^{T_2} C_p\, dT$$

FOR A REAL GAS ONLY IF P = CONST

$$= C_p \Delta T \quad \text{IF } C_p = \text{CONST}$$

ONE FINAL RELATION FOR AN IDEAL GAS

$$\Delta H = \Delta U + \Delta PV$$
$$= \Delta U + R \Delta T \quad \text{(I.G.)}$$

$$\Delta H = C_v \Delta T + R \Delta T$$

$$\Delta H = C_p \Delta T = (C_v + R) \Delta T$$

CLOSE FOR REAL GASSES AS WELL

$$\boxed{C_p = C_v + R}$$

SO FOR OUR

ISOTHERMAL COMPRESSION

$\Delta U = C_V \Delta T = 0$!

HENCE

$Q = + \int P dV$

$$\boxed{Q = -RT \ln \frac{P_2}{P_1}}$$

STEP 1

$$\boxed{W_{EC} = RT \ln \frac{P_2}{P_1}}$$

STEP 1

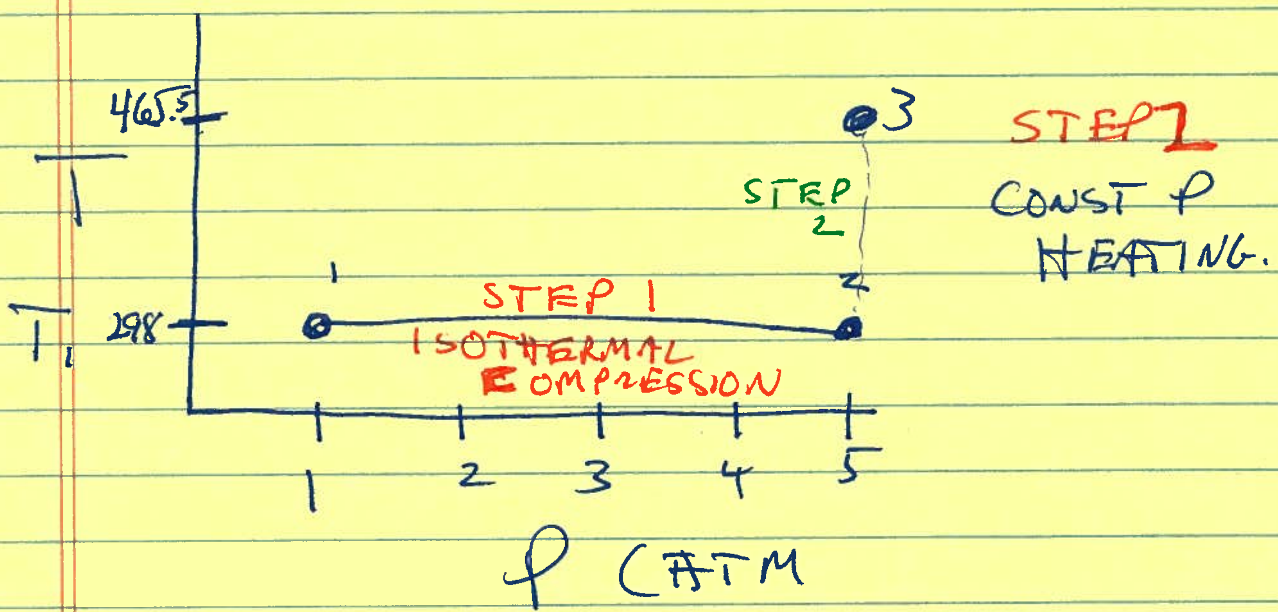
LET'S CONTINUE WITH OUR

PISTON + CYLINDER

$C_P = 30 \frac{J}{\text{MOLE-K}}$

$C_V = (30 - R) \frac{J}{\text{MOLE-K}}$

SO FAR



$$\Delta U = Q - \int P\,dV$$

P = CONST

$$\Delta U = Q - P\,\Delta V$$

WHICH TERMS CAN WE CALCULATE?

FOR AN IDEAL GAS

$$\Delta U = C_V\,\Delta T$$

$$\Delta U = (30 - 8.314)\,\frac{J}{\text{MOLE-K}}\,(465.5 - 298)$$

$$\Delta U = 3630\,\frac{J}{\text{MOLE}}$$

$Q = ??$

HOW ABOUT

$P \Delta V$?

$$W_{BC} = -P(V_3 - V_2)$$

$$= -P\left(\frac{RT_3}{P_3} - \frac{RT_2}{P_2}\right)$$

BUT, $P = \text{CONST}$

$$= -R(T_3 - T_2)$$

$$= -8.314(465 - 298)$$

FOR CONST P HEATING WORK IS OUT DOES THIS MAKE SENSE?

YES!!

$$\boxed{W_{BC} = -1390 \ \frac{J}{MOLE}}$$

FIND Q

$$Q = \Delta U + \underbrace{P\Delta V}_{(-W_{BC})}$$

$$= 3630 + 1390$$

$$\boxed{Q = 5020 \ \frac{J}{MOLE}}$$

NOW COOL AND EXPAND FROM

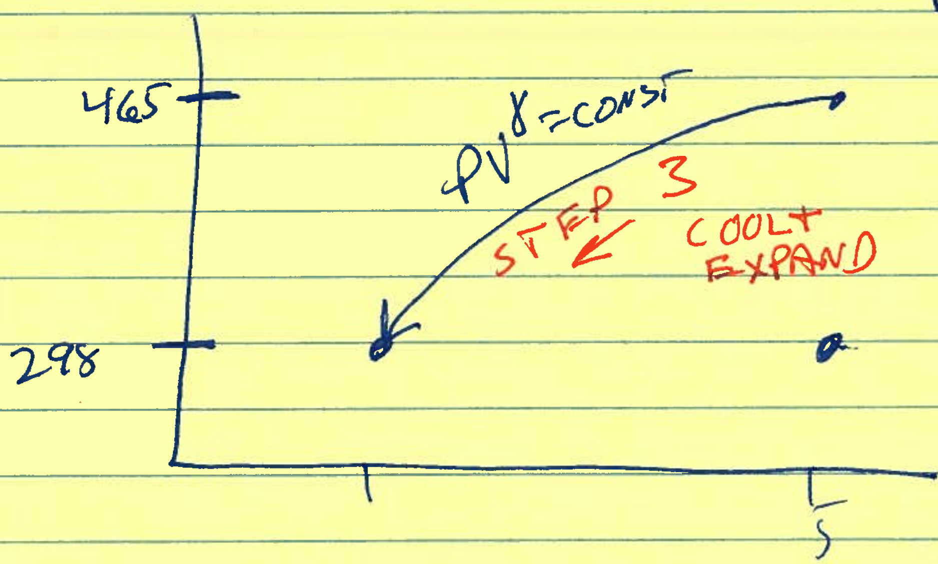
$P = 5$ ATM, $T = 465.5$ K

DOWN TO:

$P = 1$ ATM, $T = 298$ K

1 STEP SUCH THAT

$PV^{\gamma} = \text{CONST}$ $\quad \gamma = \frac{C_P}{C_V}$



$$\Delta U = Q - \int P\,dV$$

WHICH TERM CAN WE CALCULATE EASILY?

$$\Delta U = C_V \, \Delta T$$

$$\Delta U = (30 - 8.314)(298 - 465.5)$$

$$\Delta U = -3630 \ \frac{J}{MOLE}$$

$$W_{EC} = -\int P \, dV$$

WE REQUIRE:

$$P V^{\gamma} = CONST$$

$$P = \frac{CONST}{V^{\gamma}}$$

SUBS FOR P

$$W_{EC} = -\int_{V_3}^{V_1} \frac{CONST}{V^{\gamma}} \, dV$$

PULL OUT CONST

$$= -CONST \int_{V_3}^{V_1} \frac{dV}{V^{\gamma}}$$

INTEGRATE

$$= \frac{-CONST}{1-\gamma} \left(V_1^{\,1-\gamma} - V_3^{\,1-\gamma} \right)$$

BUT RECALL

REARRANGE TO ALLOW FOR BACK SUBSTITION USING $P = \frac{CONST}{V^{\gamma}}$

$$= -CONST \left(\frac{V_1}{V_1^{\gamma}} - \frac{V_3}{V_3^{\gamma}} \right)$$

$$= \frac{-1}{1-\gamma} \left(P_1 V_1 - P_3 V_3 \right)$$

BUT $PV = RT$ SO:

USE $RT = PV$

$$= \frac{-1}{1-\gamma} R(T_1 - T_3)$$

$\gamma = \frac{C_P}{C_V}$

$$= \frac{1}{\left(\frac{C_P}{C_V} - 1\right)} R \left(T_1 - T_3\right)$$

FLIP DENOMINATOR SIGN CHANGES

$C_P - C_V = R$

$$= \frac{R}{\frac{C_P - C_V}{C_V}} \left(T_1 - T_3\right)$$

$$W_{EC} = C_V (T_1 - T_3)$$

$$= -3630 \ \frac{J}{MOLE}$$

$$Q = \Delta U - W_{EC}$$

$$= -3630 - (-3630)$$

$$Q = 0 \ !$$

OBVIOUSLY THIS WAS NOT A COINCIDENCE!!

SO LET'S DO THE ACCOUNTING

STEP	ΔU	Q	W_{EC}
1 (1-2)	0	-3990	3990
2 (2-3)	3630	5020	-1390
3 (3-1)	-3630	0	-3630
	0	1030	-1030

COMMENTS:

1) WE WENT AROUND A "CYCLE" ENDING WHERE WE STARTED:

$\Delta U = 0$ BECAUSE $U(T, V)$ IS A STATE FUNCTION.

2) THE NET EFFECT OF HEAT IS 1030 J IN

Q DEPENDS ON THE PATH THAT WE TAKE.

3) THE NET WORK IS -1030 J

SO THIS CYCLE IS A "HEAT ENGINE". Q → IN
W → OUT.

2 + 3 SUGGEST THAT WE COULD LOOK FOR PATHS THAT MAXIMIZE WORK OUT FOR AN AMOUNT OF HEAT IN! b