

# THERMO NOTES

- EXTENSIVE & INTENSIVE VARIABLES
- FIRST LAW:  $dU = \delta Q + \delta W$
- ZEROETH LAW

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

$$\begin{aligned} pV^\gamma &= \text{CONST.} \\ TV^{\gamma-1} &= \text{CONST.} \\ T^\gamma p^{1-\gamma} &= \text{CONST.} \\ &\text{FOR ADIABATIC.} \end{aligned}$$

- MEASUREMENT OF TEMPERATURE

- NEED QUANTITY AS  $T \uparrow$  OR  $T \downarrow$
- NEED FIXED POINTS

IDEAL GAS THERMOMETER

BOYLE'S LAW:  $\lim_{p \rightarrow 0} (pV) = \text{CONSTANT} = f(T)$

CHARLES' LAW:  $\frac{V_{100^\circ} - V_0^\circ}{V_0^\circ}$  IS SAME  $\forall$  GAS IF  $p$  LOW (& NOT NEAR LIQUEFACTION TEMPERATURE)

$\Rightarrow$  CELSIUS TEMPERATURE:  $T_{\text{CELSIUS}} = 100 \frac{(pV)_T - (pV)_{\text{melting point}}}{(pV)_{\text{boiling point}} - (pV)_{\text{melting point}}}$  AS  $p \rightarrow 0$

- FIRST LAW IN WORDS:

ENERGY IS CONSERVED WHEN HEAT IS TAKEN INTO ACCOUNT.

•  $\delta W = -p dV$

- CONJUGATE PAIRS OF INTENSIVE & EXTENSIVE VARIABLES

-  $C_V$ :  $dU = \delta Q + \delta W$ , BUT  $V$  IS CONSTANT SO:  $\delta W = p dV = 0 \Rightarrow dU = \delta Q$

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

MONOATOMIC IDEAL GAS:  $U = \frac{3}{2} RT$

$$\Rightarrow C_V = \frac{3}{2} R$$

DIATOMIC:  $U = \frac{5}{2} RT \Rightarrow C_V = \frac{5}{2} R$  (PER MOLE)

-  $C_P \equiv \left( \frac{dQ}{dT} \right)_p$

$$\delta Q = dU - \delta W = dU + p dV$$

$$C_P = C_V + R$$

WE HAVE:  $C_V = \left( \frac{\partial U}{\partial T} \right)_V \Rightarrow$  FIND  $U(T, V)$ :

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV$$

$$\delta Q = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV + p dV$$

BACK OFF FROM INFINITESIMAL LIMIT:

$$\delta Q \approx \left( \frac{\partial U}{\partial T} \right)_V \delta T + \left( \frac{\partial U}{\partial V} \right)_T \delta V + p \delta V$$

DIVIDE BY  $\delta T$ .

$$\frac{\delta Q}{\delta T} \approx \left( \frac{\partial U}{\partial T} \right)_V \frac{\delta T}{\delta T} + \left( \frac{\partial U}{\partial V} \right)_T \frac{\delta V}{\delta T} + p \frac{\delta V}{\delta T}$$

SPECIFY A PATH.

$$\left( \frac{\delta Q}{\delta T} \right)_p \approx \left( \frac{\partial U}{\partial T} \right)_V \left( \frac{\delta T}{\delta T} \right)_p + \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\delta V}{\delta T} \right)_p + p \left( \frac{\delta V}{\delta T} \right)_p$$

TAKE LIMIT AGAIN:

$$C_P = \left( \frac{dQ}{dT} \right)_p = \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p =$$



$$= C_V + \left[ \left( \frac{\partial U}{\partial V} \right)_T + p \right] \left( \frac{\partial V}{\partial T} \right)_p$$

FOR 1 MOLE:  $pV = RT \Rightarrow \left( \frac{\partial U}{\partial T} \right)_p = R \Rightarrow C_p = C_V + R$  (PER MOLE)

## JOULE VS ISOTHERMAL EXPANSION



### JOULE

PULL PISTON OUT VERY QUICKLY.  
IMAGINE THAT YOU PULL OUT QUICKER THAN AVG TIME B/TWN HITS OF ATOMS & PISTON, SO GAS "DOESN'T NOTICE".

SO IT IS FREELY EXPANDING.  
NO MOVING BOUNDARY AS FAR AS GAS IS CONCERNED.  $\Rightarrow$  NO WORK EXCHANGE W/ SURROUNDINGS

INSULATED ENCLOSURE  $\Rightarrow$  FIRST LAW  $\Rightarrow \Delta U = 0$

FROM:  $V = V_1$  TO:  $V = V_2$   
 $T = T_1 \Rightarrow T = T_2$  BEC  $U = U(T)$  ONLY,

$$\Delta U = 0 \Rightarrow \Delta T = 0$$

TO RESTORE ORIGINAL STATE, COMPRESS GAS ISOTHERMALLY.

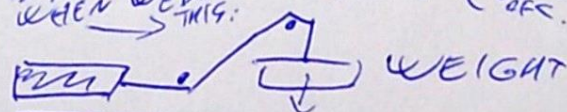
$$\text{WORK: } \int p dV$$

IF  $T$  IS CONSTANT, HEAT REJECTED TO SURROUNDINGS (SAME AMOUNT AS WE DID WORK ON IT) (FROM FIRST LAW &  $U = U(T)$ )

EXPANSION  
- WE DO WORK  
- GAS COMPRESSED & REJECTS THIS WORK TO SURROUNDINGS

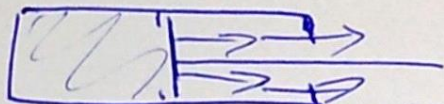
NET EFFECT: WE CONVERTED

NET EFFECT IS SAME AS WHEN WE DO THIS:  $W$  WORK TO  $Q$  HEAT ( $W = Q$ )



ROUGH SURFACE NOT REVERSIBLE if you pull it, cannot just go back (without doing work again)

### ISOTHERMAL



PULL OUT SLOWLY

AS WE PULL OUT, MOLECULES HIT THE PISTON, THEY SLOW DOWN & TRANSFER WORK TO US.

$$\text{THIS MUCH: } W = \int p dV = \int_{V_1}^{V_2} nRT \frac{1}{V} dV = nRT \ln \left( \frac{V_2}{V_1} \right)$$

DURING EXP.:

- SURROUNDINGS HAVE RECEIVED WORK  $W$

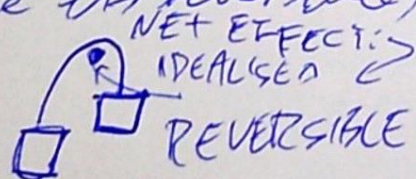
- SURROUNDINGS HAVE GIVEN UP HEAT  $Q$  ( $Q = W$ )

TO RESTORE SYS, WE DO WHAT WE DID IN FREE (IE JOULE) EXP.:

- WORK ON SYS
- EXTRACT HEAT FROM SYS (TO KEEP  $T = 0$ )

WORK IN  $W$   
HEAT OUT:  $Q$

NO TRACE OF OVERALL PROC ON SYS OR SURROUNDINGS (ie it's reversible)

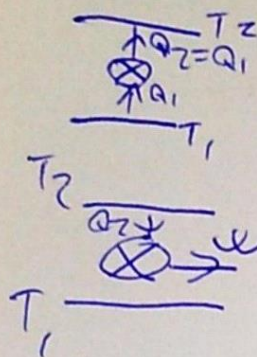




## SECOND LAW

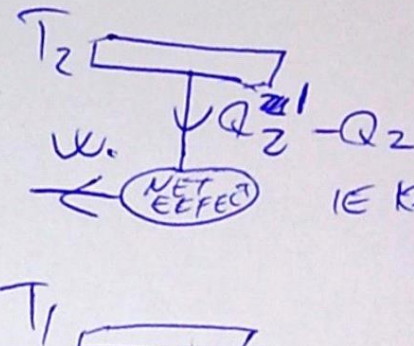
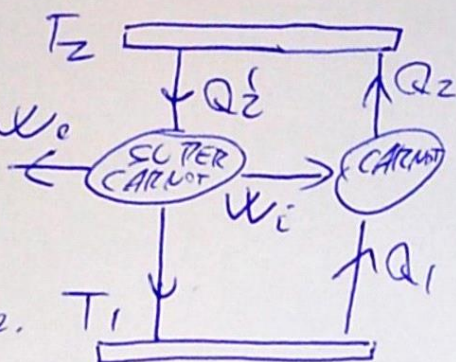
Clausius Form: "NO PROCESS IS POSSIBLE WHOSE ONLY EFFECT IS TO TRANSFER HEAT FROM A COLDER BODY TO A HOTTER BODY."

KELVIN'S FORM: "NO PROCESS IS POSSIBLE WHOSE ONLY EFFECT IS THE COMPLETE CONVERSION OF HEAT INTO WORK."



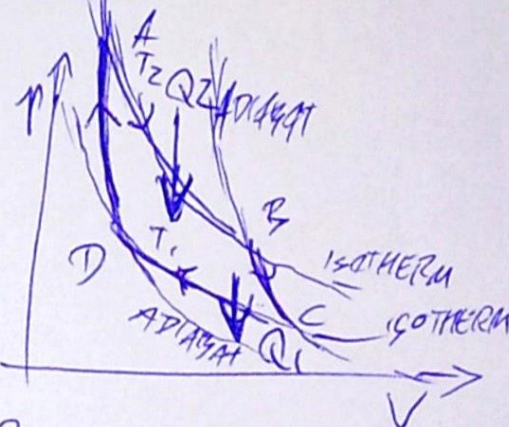
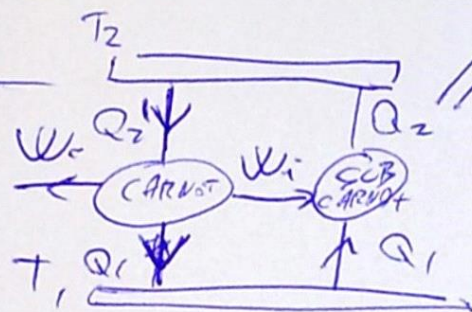
## CARNOT THM

No engine operating between two reservoirs can be more efficient than a Carnot engine.



IE KELVIN VIOLATOR

## CARNOT THM COROLLARY



## EFFICIENCY OF A CARNOT CYCLE

$$\eta = \frac{\text{WORK DONE BY SYS}}{\text{HEAT ABSORBED}} = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2} = 1 - \frac{Q_1}{Q_2}$$

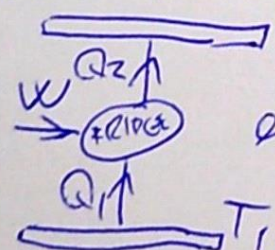
FOR 1 MOLE OF IDEAL GAS:  $Q_2 = \int_{V_A}^{V_B} P dV = \int_{V_A}^{V_B} \frac{RT_2}{V} dV = RT_2 \ln \frac{V_B}{V_A}$

ADIABATIC EXP<sup>AN</sup> EQ.:  $TV^{\gamma-1} = \text{CONSTANT}$

LIKEWISE:  $Q_1 = RT_1 \ln \frac{V_D}{V_C}$

## REFRIGERATOR

### CARNOT IN REVERSE



$$T_2 V_B^{\gamma-1} = T_1 V_C^{\gamma-1} \quad \& \quad T_2 V_A^{\gamma-1} = T_1 V_D^{\gamma-1}$$

$$\frac{V_B}{V_C} = \frac{V_A}{V_D} \Rightarrow \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

$$\eta = 1 - \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2}$$

## HEAT PUMP

SAME AS A FRIDGE BUT HOUSE IS WHERE HEAT IS PUT (NOT EXTRACTED)

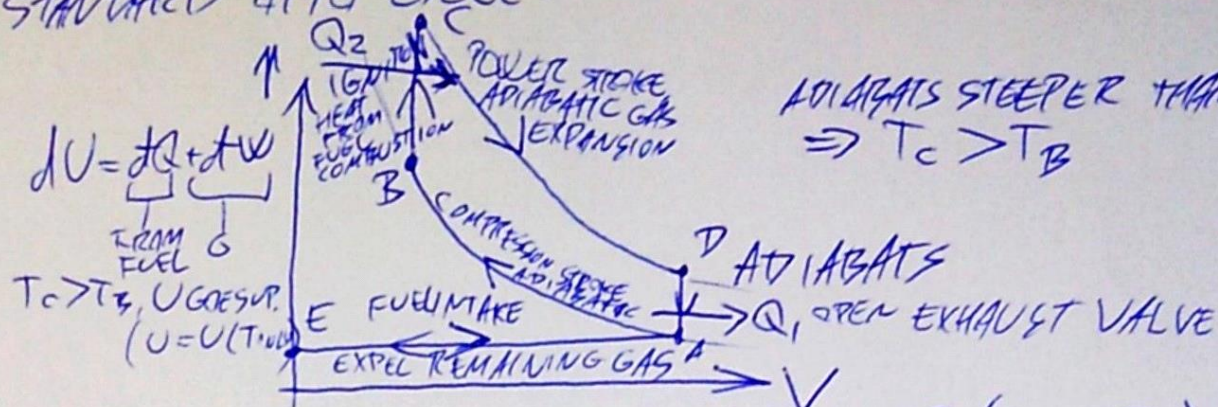
$$\eta = \frac{Q_2}{W} = \frac{Q_2}{Q_2 - Q_1} = \frac{T_2}{T_2 - T_1} > 1$$

TRUE FOR ALL REVERSIBLE HEAT ENGINES (NOT JUST FOR IDEAL GAS VERSIONS)



- THERMODYNAMIC TEMPERATURE SCALE WITH CARNOT ENGINES

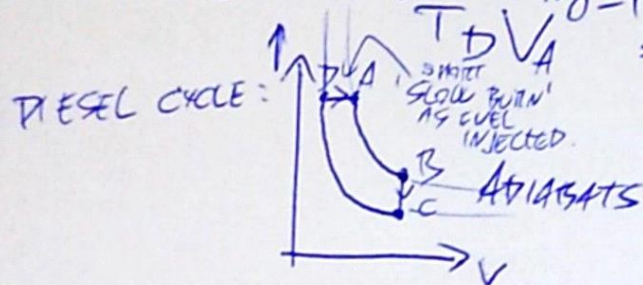
- AIR STANDARD OTTO CYCLE.



$$Q_2 = C_V (T_C - T_B) \quad Q_1 = C_V (T_D - T_A)$$

$$\eta = \frac{Q_2 - Q_1}{Q_2} = 1 - \frac{Q_1}{Q_2} = 1 - \frac{T_D - T_A}{T_C - T_B}$$

ADIABATIC EXPANSION EQ AGAIN:  $\gamma - 1$



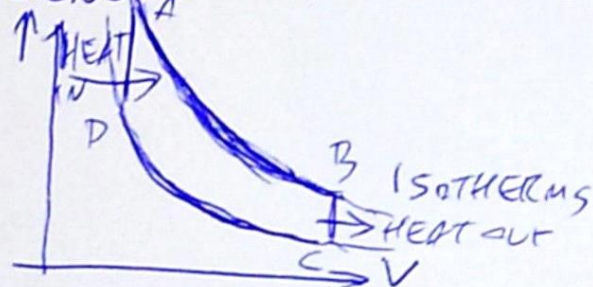
$$T_D V_A^{\gamma-1} = T_C V_B^{\gamma-1} \Rightarrow T_D = T_C \left( \frac{V_B}{V_A} \right)^{\gamma-1} = T_C \left( \frac{V_A}{V_B} \right)^{1-\gamma}$$

$$\text{LIKEWISE: } T_A = T_B \left( \frac{V_A}{V_B} \right)^{1-\gamma}$$

$$r = \frac{V_A}{V_B}$$

COMPRESSION RATIO

STEELE ENGINE



ENTROPY IN REVERSIBLE CHANGES

