

Observations from Joule's Experiments

- 1) A closed system (control mass) undergoing an adiabatic change of state (new T in Joule's case) requires the same expenditure of work, regardless of the type of work
- ⇒ a state variable (U) must exist which is related to work (energy transfer), e.g., $W=U_2-U_1$ as the system adiabatically goes from state 1 to state 2
- 1) From experience (experiments), the same change of state can be accomplished (without work) by putting the body in contact with a hotter body, i.e., another mode of energy transfer is **heat transfer**

1st Law (Control Mass)

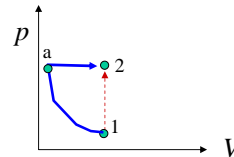
• Postulate

- there exists a function of state U , called internal energy (an extensive property)
- for an infinitesimal state change (with $dKE=dPE=0$) in a closed system sign convention here

$$dU = \delta Q + \delta W$$

$\delta Q > 0$ if heat xfer into system
 $\delta W > 0$ if work done on system

- Since U is state variable (property of matter), dU is exact differential; $\int_1^2 dU = U_2 - U_1$
- $\delta Q, \delta W$ are inexact; **not properties** but depend on path between states
 - e.g., no work in vertical path $\int_1^2 \delta W \neq \text{Ⓜ} - \text{Ⓜ}$



1st Law: Integral Form

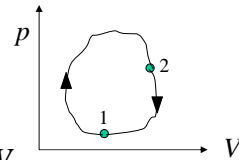
- So undergoing change between states

$$U_2 - U_1 = \Delta U_{12} = Q_{12} + W_{12}$$

- For a cyclic process

$$\oint dU = U_1 - U_1 = 0 = \oint \delta Q + \oint \delta W = Q + W$$

$$\therefore Q = -W$$



- if there is net work produced in cycle, then there must be net heat transfer into system

⇒ no perpetual motion machines

Fluid Compression (pV) Work

- Amount of energy transfer as work from surroundings into fluid

$$\delta W = -pdV \quad \begin{array}{l} \text{same sign convention} \\ \text{compression } \delta V < 0, \text{ work in } (\delta W > 0) \end{array}$$

- If compression/expansion work only (& no KE, PE change)

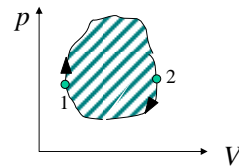
$$dU = \delta Q - pdV$$

- For cyclic process

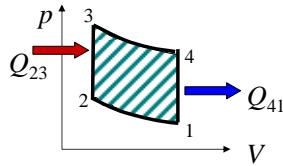
$$Q = -W = \oint pdV$$

$$= \int_1^2 pdV + \int_2^1 pdV$$

$$Q = \int_1^2 pdV - \int_1^2 pdV \quad \text{shaded area}$$



Example: Otto Cycle



Shaded Area

= Net Heat Transfer in
($Q_{23} - Q_{41}$)

= Net Work done by system
($W_{34} - W_{12}$)

- 1→2 Compression (adiabatic)
- 2→3 Heat transfer into fluid
 - “from” combustion (no work, $dV=0$)
- 3→4 Expansion (adiabatic)
- 4→1 Exhaust and refill strokes
 - “=” heat transfer out, “ideally” no net work

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Examples: Combustion Problems

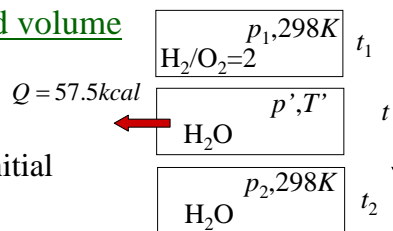
- **Combustion (CM) at fixed volume**

– $dV=0 \Rightarrow dU = \delta Q$

– or $\Delta U_{12} = Q_{12}$

– by cooling products to initial (reactant) temperature

$$U_2 - U_1 = Q \equiv Q_V$$



- $Q_V \equiv$ **heat of reaction (combustion) at constant vol.**

– like state function (since $W=0$)

- For our case $U \left\{ H_2(g) + \frac{1}{2} O_2(g) \right\} = U \{ H_2O(g) \} + 57.5kcal$

– $Q_V = -57.5kcal/mol_{H_2O} < 0 \Rightarrow$ *exothermic*
1 kcal = 4.186 kJ

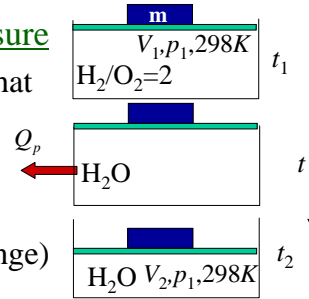
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Examples: Combustion Problems

- Combustion (CM) at fixed pressure

- assume reaction slow enough that we can keep const. p
- again extract heat to cool products to initial T
- what is Q now (note V can change)



- 1st Law

$$dU = \delta Q - pdV \Rightarrow \Delta U_{12} = Q_p - p\Delta V_{12}$$

if Perf. Gas $pV = n\bar{R}T$

$$d(pV) = pdV = d(n\bar{R}T) = \bar{R}Tdn \quad 1H_2O - (1H_2 + \frac{1}{2}O_2)$$

$$p\Delta V_{12} = \bar{R}T\Delta n_{12} = -\bar{R}T(n_{H_2O}/2)$$

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Examples: Combustion Problems

- Combustion (CM) at fixed pressure

- so work DONE on system per mole H_2O made

$$W = -p\Delta V \quad W/n_{H_2O} = \frac{1}{2}\bar{R}T$$

- to get Q , need ΔU ; $Q_p = \Delta U_{12} - W_{12}$

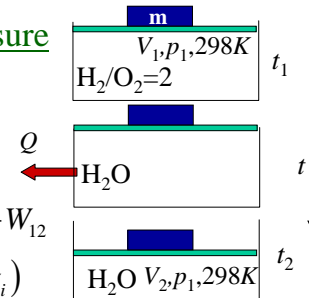
$$\Delta u = \frac{\Delta U}{M} = f(v, T, \chi_i) = f(T, \chi_i) \quad \text{Perf. Gas}$$

- but T and composition same as const. vol. case, so for 1 mole H_2O produced

$$Q_p = \Delta U_{12} - W_{12} = Q_v - \frac{1}{2}\bar{R}T = -57.5kcal - \frac{1}{2}\left(1.956 \frac{cal}{molK}\right)298K$$

$$Q_p = -57.8kcal/mol_{H_2O}$$

because less moles of products, final volume is less, work done TO gas, and more energy must be extracted by heat transfer to reach 298K



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