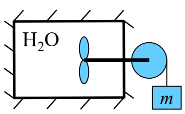
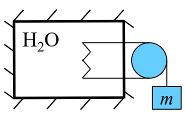
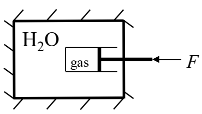
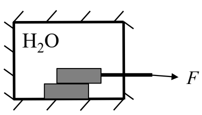
First Law of TD

- This postulate added internal energy to the existing mechanical concepts of kinetic and potential (e.g., gravitational) energy
  - example for isolated system, $dE = dU + dKE + dPE = 0$
- Empirical Evidence
  - original formulation based on experiments in 1800's, especially those of Joule (1843-1848)
  - Joule performed 4 experiments looking at different ways of using work to increase the temperature of a fixed mass of liquid water at 1 atm in an "adiabatic" enclosure

Joule's Four Experiments

- Based on no change in KE/PE of water

	Method	$\boldsymbol{W}$ (ft lb_f)	
	Direct work	773	1 lb_m of water raised by 1°F at room T
	Work via electricity generation *(using poor generator)*	883	
	Work (compression) on internal gas	795	**Average of closest 3 values** 781 ft lb_f/lb_m°F
	Work via friction	775	**Accepted value today** 778 ft lb_f/lb_m°F (= 4.184 J/kgK)

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

2) 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)

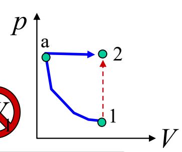
- **Postulate**
  - there exists a function of state ***U***, called internal energy (an extensive property)
  - for an infinitessimal state change (with d*KE*=d*PE*=0) in a closed system

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

sign convention here
$\delta Q>0$ 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; $\int_1^2 dU = U_2 - U_1$
- δQ, δW are inexact; not properties but depend on path between states
  - no pdV work in vertical path
  - but work in other paths

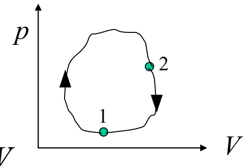
$\int_1^2 \delta W \neq W - W$



1^{st} 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 (*pdV*) Work

- Amount of energy transfer as work from surroundings into fluid

$$\delta W = -pdV$$

same sign convention
compression $\delta V<0$, work in ($\delta W>0$)

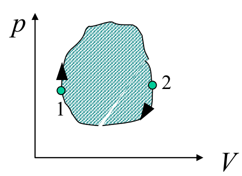
- If compression/expansion work only (& no KE, PE change)

$$dU = \delta Q - pdV$$

  – if also cyclic process

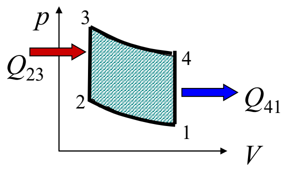
$$Q = -W = \oint pdV$$

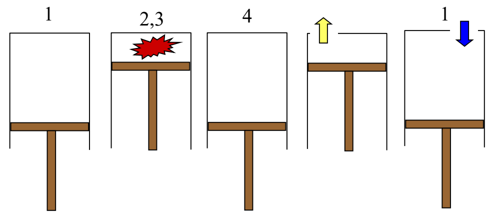
$$= \int_1^2 pdV + \int_2^1 pdV$$



$$Q = \int_1^2 pdV - \int_1^2 pdV$$ ***shaded area***

Example: Otto Cycle





Shaded Area

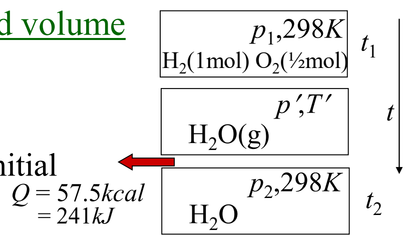
= Net Heat Transfer in (Q_{23}-Q_{41})

= 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

Examples: Combustion Problems

- Combustion (CM) at <u>fixed volume</u>
  - $dV=0 \Rightarrow \; dU=\delta Q$
  - 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 volume**
  - like state function (since W=0)
- For our case $U\left\{H_2(g)+\frac{1}{2}O_2(g)\right\} = U\{H_2O(g)\} + 57.5kcal$
  - $Q_V = -57.5\ kcal/mol_{H_2O}$ $<0 \Rightarrow$ *exothermic*

1 *kcal*=4.186 *kJ*

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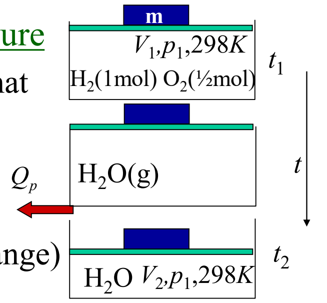
Examples: Combustion Problems

- Combustion (CM) at fixed pressure
  - assume reaction slow enough that we can keep constant p
  - again extract heat to cool products to initial T
  - what is Q now? (note V can change)



- 1[st] Law

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

if thermally perfect gas (tpg) $pV = n\bar{R}T$

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

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

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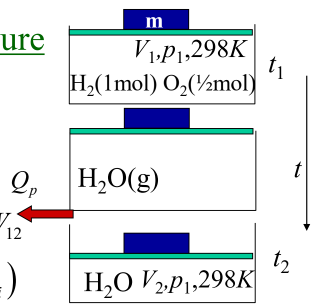
Examples: Combustion Problems

- Combustion (CM) at fixed pressure
  - so work DONE on system per mole H_2O made

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



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

$$\Delta u = \frac{\Delta U}{m} = f(v,T,\chi_i) = f(T,\chi_i)$$

for tpg

  - but T and composition same as constant volume case, so for 1 mole H_2O produced

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

$$Q_p = -57.8\,kcal/mol_{H_2O} = -241.8kJ/mol$$

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