ENERGY

KINETIC ENERGY

POTENTIAL ENERGY

$U \leftarrow$ INTERNAL ENERGY

$U \leftrightarrow$ vibrations, rotations, chemical bonds

$\boxed{\text{FIRST LAW}}$ $\Delta U_{\text{UNIVERSE}} = 0$

$$\Delta U_{SYS} + \Delta U_{SUR} = 0$$

FOR SYSTEMS WITH NO CHEMICAL RXN
NO PHASE TRAN

$$\Delta U = q + w$$

q = heat

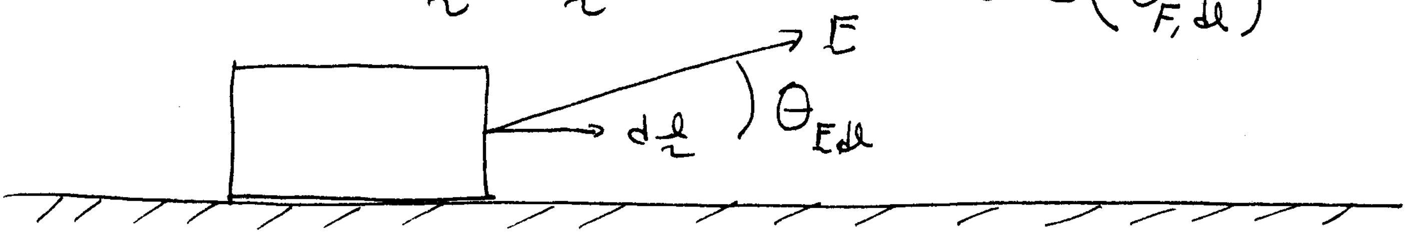
w = work

$q \equiv$ heat $\equiv$ flow of energy ACROSS A BOUNDARY DUE TO A TEMPERATURE DIFFERENCE

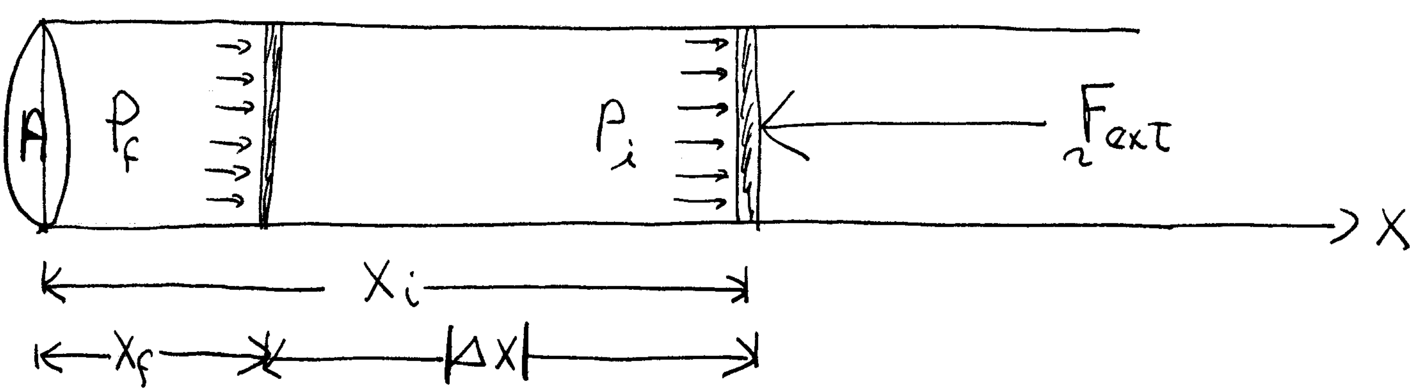
WORK

FROM CLASSICAL MECHANICS, WORK ON A SYSTEM BY A FORCE $\underset{\sim}{F}$ IS

$$đW \equiv \underset{\sim}{F} \cdot d\underset{\sim}{l} = |F|\,|dl|\,\cos(\theta_{F,dl})$$



LET US CONSIDER A GAS CONTAINED IN A CYLINDER BY A CONSTANT EXTERNAL FORCE.



IN A COMPRESSION $\underset{\sim}{F}_{ext}$ IS IN THE SAME DIRECTION AS ΔX. THUS

$$\cos(\theta_{F,dl}) = \cos(0) = 1,$$

AND WE HAVE

$$\Delta W = |F_{ext}|\,|\Delta X|$$

BUT IN A COMPRESSION $\Delta X < 0$, THUS WE CAN WRITE

$$\Delta W = - |F_{ext}| \, \Delta X$$

SINCE $|\Delta X| = - \Delta X$.

IN AN EXPANSSION, THE ANGLE BETWEEN $\underset{\sim}{F}_{ext}$ AND $d\underset{\sim}{\ell}$ IS π, AND $\cos(\theta_{F/d\ell}) = -1$. MOREOVER, IN THIS CASE $\Delta X > 0$. THUS WE HAVE

$$\Delta W = - |F_{ext}| \, |\Delta X|$$

$$= - |F_{ext}| \, \Delta X.$$

NOTICE THAT THE FORCE HAS TO CONSTRAIN THE GAS INTO THE PISTON. OTHERWISE, WE DO NOT HAVE A SYSTEM.

WE CAN SAY THAT $\underset{\sim}{F}_{ext}$ IS A POSITIVE IF CONSTRAINS THE GAS INTO THE CYLINDER AND NEGATIVE IF IT DOES NOT. IN THIS CASE, WE WILL NEVER HAVE A SYSTEM AT EQUILIBRIUM, NO MATTER HOW LONG WE WAIT.

IF WE CONSIDER THE AREA, A, OF THE PISTON

$$\Delta W = - \left(\frac{|F_{ext}|}{A} \right) A \Delta X .$$

BUT $|F_{ext}|/A = P_{ext}$ AND $A \Delta X = \Delta V = V_f - V_i$. THE FINAL EXPRESSION FOR P-V WORK IS GIVEN BY

$$\Delta w = - P_{ext} \Delta V.$$

NOTICE THAT $\Delta W > 0$ ON A COMPRESSION $(V_f < V_i)$ AND $\Delta W < 0$ IN AN EXPANSSION $(V_f > V_i)$.

THE UNITS WILL BE

$$atm \cdot L = 1.013 \times 10^5 \text{ newton } m^{-2} (10^{-3} m^3)$$

$$atm \cdot L = 101.3 \text{ newton } m = 101.3 J$$

If WE NOW CONSIDER INFINITESIMAL DISPLACEMENTS, WE GET AN EXPRESSION FOR IFINITESIMAL WORK

$$đw = - P_{ext} dV,$$

WHERE $đw$ STANDS FOR AN INCOMPLETE DIFFERENTIAL.

HEAT (FORM OF ENERGY)

FOR A SYSTEM $q > 0 \Rightarrow \Delta T > 0$

$q < 0 \Rightarrow \Delta T < 0$

$$\boxed{\begin{array}{l} 1\,g\ H_2O \leftrightarrow 1\ cal \Rightarrow \Delta T = 1\ ^{\circ}C \\ 1\ cal = 4.18\ J\ g^{-1}K^{-1} \end{array}}$$

$$\boxed{q \equiv C\,\Delta T}$$

$$C = \frac{\Delta q}{\Delta T}$$

$$\boxed{C = \frac{dq}{dT}}$$

$$dq = C\,dT$$

$$\boxed{q = \int_{T_i}^{T_f} C(T)\,dT}$$

$C \rightarrow \quad C_p$ CONSTANT P

C_V CONSTANT V

$$C_p = \lim_{\Delta T \to 0} \left(\frac{q_p}{\Delta T} \right)$$

$$C_V = \lim_{\Delta T \to 0} \left(\frac{q_V}{\Delta T} \right)$$

$$C_p > C_V$$

A P=CONST THE SYSTEM NEEDS TO DO WORK AND INCREASE ITS TEMPERATURE SO

$$q_p > q_v$$

FOR THE SAME FINAL TEMPERATURE.

ALTHOUGH

$$\Delta q \neq q_f - q_i = \int_i^f đq$$

AND

$$\Delta W \neq W_f - W_i = \int_i^f đW$$

THE COMBINATION

$$\Delta U = \Delta q + \Delta W = U_f - U_i$$
$$= \int_i^f dU$$

REVERSIBLE PROCESS $\Rightarrow$ THAT THE SYSTEM AND ITS SURROUNDINGS ARE IN THERMAL EQUILIBRIUM

$\Leftrightarrow$ QUASI STATIONARY

STATE FUNCTION OR PATH INDEPENDENT FUNCTION

DEFINITION

IF ΔU DEPENDS ONLY ON THE INITIAL AND FINAL CONDITIONS, U IS A STATE FUNCTION

$$\boxed{\Delta U = \int_i^f dU = U_f - U_i}$$

COROLLARY $\Delta U = 0$ FOR A CLOSED PATH.

$$\Delta U = \oint dU = 0$$

WORK AND ~~HEAT~~ ARE NOT STATE FUNCTIONS BUT

$$q + w = U$$

IS A STATE FUNCTION.