FRI 9/7/01 ①

Energy Exchange

Work ≡ $f \times d$

$P \times dV$

other forms (electrical, ...)

Convention: For this book, but not all...

$w > 0$ Surroundings do work on system

$w < 0$ System does work on surrounding

Cases of $w = f \times d$

Hook's Law - extending a spring
(what's this a model for ??)
— bond stretching

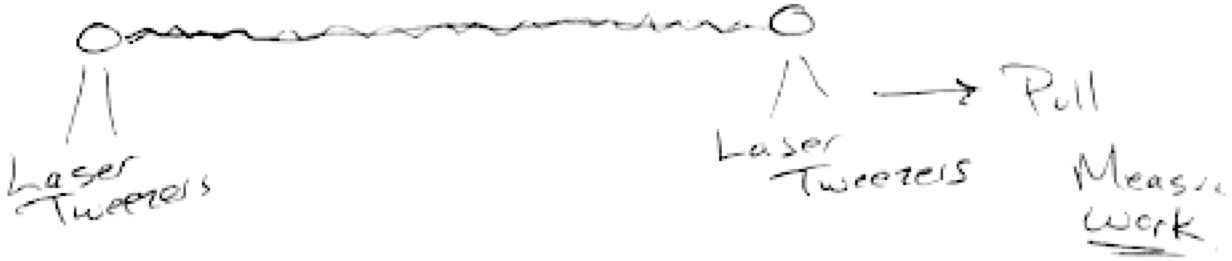
$$f = -k(x - x_0) \leftarrow \text{force varies with distance}$$

$$\therefore\ w = -\int f\,dx = -\int_{x_1}^{x_2} k\,(x - x_0)\,d(x - x_0$$

$=$

Real-life experiments w/ Hooke's Law

Pulling on single molecules of DNA or microtubules



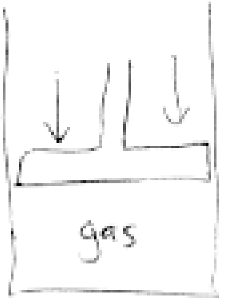
PdV Work ⇒ Piston setup

$$w = -\int_{V_1}^{V_2} P_{ex}\, dV$$

↑ work done **on** the system

3D Force

3D "Distance"



Sign convention and common sense

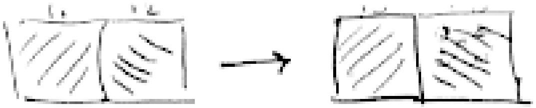
For the surroundings (me) to compress the system (gas), I must do work on the system

$$w = -\int \overset{P}{(+)}\,\overset{dV}{(-)} = (+)$$

Work against gravity

$$w = mg\,\Delta h$$

What convention?



<u>Heat</u> ⇛ Spontaneous flow of <u>energy</u> from a warm body in contact with a cold one

Heat is <u>positive</u>, if heat transfers <u>to</u> the system

(again, "system-centric)

For a <u>closed</u> system, transfer of a small amount of heat <u>into</u> the system raises the <u>temperature</u> of the system
(no <u>matter</u> xfer)

The <u>ratio</u>

$$\frac{dq}{dT} = \frac{\text{heat transfered}}{\text{rise in temperature}} = \frac{\text{heat in}}{\text{change in temperature}}$$

$$= \text{Heat capacity} = C = \frac{dq}{dT}$$ ← Kelvin or Celsius

C is <u>extensive</u>, ie. depends on the total amount

$\bar{C}$ = <u>molar</u> heat capacity (per mole) $\qquad C = n\bar{C}$

Specific Heat capacity of pure, liquid water near RT = $1 \frac{cal}{Kg}$
↓
(per gram)

The heat capacity of a reaction/chemical can tell us about the molecular structure/ interactions

$$\frac{dq}{dT} = C \quad \rightarrow \quad q = \int_{T_1}^{T_2} C \, dT$$

IF C = constant from $T_1 \rightarrow T_2$

THEN

$$q = C \Delta T$$

FIRST LAW OF THERMO (again!)

Total energy of (system + surroundings = universe) is constant.

For a closed (no matter xfer, but E xfer OK) system, if heat and work are the only forms of energy exchange, then

$$\Delta E = q + w$$

(Watch out: $\Delta E \neq q - w$)

Change in energy of the system

heat in

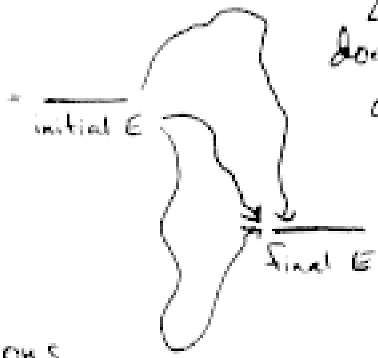
work done on (or in)

What is ΔE for an isolated system? $\boxed{0}$!

More definitions

State variables → don't depend on how the system got there.

examples, P, V, T, E $\qquad$ $H = E + PV$



ΔE does not depend on the path

When we want to calculate a change, we choose the path that is easiest to measure/calculate

Useful restrictions

$\Delta P_{sys} = 0$	isobaric
$\Delta T_{sys} = 0$	iso thermal
$\Delta V_{sys} = 0$	iso choric
$\Delta q = 0$	adiabatic
Δ everything $= 0$	cyclic

We can also talk about the heat capacity of a process/reaction

e.g. Phase change

(melting)

Heat of freezing (will be enthalpy of freezing)
Heat of vaporization (boiling).
(condensation)

Heat xfer necessary to change 1 mol of species.

Tells us something about the molecules in the two phases

Often refer to C_p (at constant pressure)
or C_V (" " volume)

q does depend on the path.

$$q_P = \int C_p \, dT \approx C_p \Delta T$$

$$q_V = \int C_V \, dT \approx C_V \Delta T$$

For most solids and liquids, $C_p \approx C_V$

At constant V, $P dV = w_V = 0$

$$w_p = -P(V_2 - V_1)$$

Skipped 9/7

Book talks about calculating changes ~~&~~
$P_1, V_1, T_1 \rightarrow P_2, V_2, T_2$
by choosing combinations of simple paths.

Define

$$\Delta H = \Delta(E + PV)$$
$$= \Delta E + \Delta(PV)$$

book shows that

$$\Delta H = n \bar{C}_p (T_2 - T_1)$$

more generally

$$\Delta H = n \int_{T_1}^{T_2} \bar{C}_p \, dT$$

We'll often see
$\Delta H = \int_{T_1}^{T_2} C_p \, dT$

For a closed system, and an isobaric process (and only PV work)

$$\Delta H = \Delta E + \Delta(PV)$$

$$= \Delta E + P\Delta V \quad \text{(isobaric)}$$

$$= q_p + w_p + P\Delta V \quad \text{(1st law)}$$

$$= q_p - P\Delta V + P\Delta V \quad \text{(definition of work)}$$

$$\Delta H = q_p$$

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weating:
Evaporation of water on your arm

$$\begin{tikzcd}
H_2O(l),\ T_2 = 35^\circ C,\ P = 1\text{ atm} \arrow[r, "?"] \arrow[d, "\text{Const P}", "\text{Change temp but not phase, Heat cap } H_2O(l)"'] & H_2O(g),\ T_2 = 35^\circ C,\ P = 1\text{ at} \\
H_2O(l),\ T_1 = 100^\circ C,\ P = 1\text{atm} \arrow[r, "\Delta H @ 100^\circ C", "\text{Change phase, but not Temp}"'] & H_2O(g),\ T_1 = 100^\circ C,\ P = 1\text{ at} \arrow[u, "\text{Heat Cap } H_2O(g)", "\text{Const P} \quad \text{Change te but not phas,}"']
\end{tikzcd}$$