

Chapter 2 → Energy is Conserved (1st Law)

State variables, functions

 Δ Energy \Rightarrow heat and work

System, surrounding, universe

Work \Rightarrow spring, piston, current

closed vs. open system

Simplest \rightarrow P.V.

Heat capacities

Enthalpies ΔH

Phase changes

Thermo - heat/energy

dynamics - change, movement (originally - power, strength)

1st LAW - Energy is conserved (really: mass/energy)2nd LAW - Entropy of an isolated system always increases3rd LAW - Entropy of any pure, perfect crystal is ϕ at $0K$ (absolute ϕ).Entropy \rightarrow disorder, randomness (will see more later)

This all speaks of bulk properties, what happens with large numbers of particles

Statistical thermodynamics shows us that this all follows logically from probability.

MECHANISMS OF ENERGY CONSERVATION \Rightarrow

WE HAVE TO BE QUANTITATIVE :

DEFINITIONS:

SYSTEM: WHAT WE'RE INTERESTED IN

SURROUNDINGS: EVERYTHING ELSE

UNIVERSE = SYSTEM + SURROUNDINGS

1st LAW \Rightarrow TOTAL ENERGY OF SYSTEM + SURROUNDINGS
DOES NOT CHANGE

Energy may be transferred from system \leftrightarrow surroundings
and can be interconverted between different
kinds of energy, but the total must remain
constant.

TRANSFERS OF ENERGY \equiv Heat \rightarrow thermal
Work \rightarrow another way to xfer energy

It is changes of energy which interest us,
So it is heat and work which interest us.

MORE
DEFINITIONS

OPEN SYSTEM

Can exchange both matter
and energy w/ system

CLOSED SYSTEM

Can exchange energy
but not matter

ISOLATED SYSTEM

No exchange
of any
kind

Work - xfer of energy

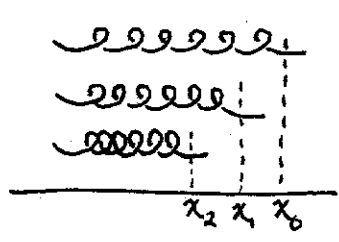
IMPORTANT

- 1) Done by the surroundings, on the system (+)
energy of system increases (xferred from surroundings)
- 2) Done by the systems, on the surroundings (-)
energy of system decreases

Work can be movement against a force

$$W = F \Delta x = \int f dx$$

Compress a Spring



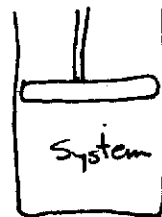
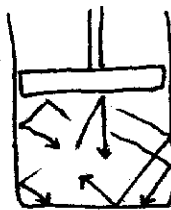
x_0 = relaxed length ($F = 0$)

$$f = k(x - x_0)$$

$$\begin{aligned}
W &= \int_{x_1}^{x_2} k(x - x_0) dx = k \int_{x_1}^{x_2} (x - x_0) dx \\
&= k \left[\frac{1}{2} x^2 - x_0 x \right]_{x_1}^{x_2} \\
&= k \left[\frac{1}{2} (x_2^2 - x_1^2) - x_0 (x_2 - x_1) \right] \\
&= k \left[\frac{(x_2 - x_1)(x_2 + x_1)}{2} - x_0 (x_2 - x_1) \right] \\
&= k(x_2 - x_1) \left[\frac{x_2 + x_1}{2} - x_0 \right]
\end{aligned}$$

Analogy to muscle fibers?

Similarly: $P \Delta V$



Instead of force \times displacement in one direction,
we have pressure \times Δ Volume
(Force/area)

$$W = - \int_{V_1}^{V_2} P_{op} dV$$

P_{op} = opposing pressure

Why negative?

Compression \equiv decrease in volume = work done on system
(-) (+)

If $P \approx$ constant, the integral is easy.

$$W_p = - P_{op} (V_2 - V_1) \Rightarrow \text{Work done on the system}$$

at constant pressure
(to simplify integral)

Check: Compression $\Rightarrow V_2 < V_1$

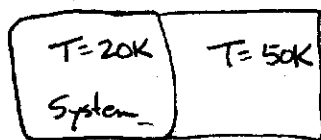
$\therefore W_p \equiv$ positive

Exercise:

Work through the examples.

Gravity, electrical, friction

HEAT - Xfer of energy spontaneously



Heat xferred to the system

energy of system increases (E of surroundings decreased)

Heat xferred from the system

energy of system decreases.

How To DESCRIBE → Heat capacity of the system

$$q = \text{heat (xferred)} = \int_{T_1}^{T_2} C dT = C (T_2 - T_1)$$

↑ if C is temperature-independent

FOR PURE CHEMICAL SUBSTANCE

MOLAR HEAT CAPACITY = heat capacity per mole

Table 2.1 lists common

VARIABLES OF STATE

We just saw how the energy transferred can be calculated by knowing how one got from state A to state B.

Often (i.e. for state variables) you don't need to know how.

State variables describe the state of the system.

Examples P, V, T, E, n

and any simple combination of the above

e.g. $H = \underbrace{E + PV}_{\text{state variables}}$

EQUATIONS OF STATE

Examples

$$PV = nRT$$

← all are state variables (or constants)

Stopped 9/10