Chapter 2  → Energy is Conserved (1st Law)

State variables, functions
State, surrounding, universe
Closed vs. open system

Heat capacities
Enthalpies $\Delta H$
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 increases
3rd LAW - Entropy of any pure, perfect crystal is 0
          at 0K (absolute 0).

Entropy → 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 →
WE HAVE TO BE **QUANTITATIVE**:

**DEFINITIONS:**

**SYSTEM:** WHAT WE'RE INTERESTED IN
**SURROUNDINGS:** EVERYTHING ELSE

UNIVERSE = SYSTEM + SURROUNDINGS

1st LAW ⇒ ** TOTAL ENERGY OF SYSTEM + SURROUNDINGS DOES NOT CHANGE **

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

**TRANSFERS OF ENERGY** = Heat → thermal  
Work → 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

1) Done by the surroundings, on the system (energy of system increases (xfered from surroundings)

2) Done by the system, on the surroundings (energy of system decreases)

Work can be movement against a force.

\[ \omega = F \Delta x = \int f \, dx \]

\( x_0 = \) relaxed length \((F = 0)\)

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

\[ \omega = \int_{x_i}^{x_2} k(x-x_0) \, dx = k \int_{x_i}^{x_2} (x-x_0) \, dx \]

\[ = k \left[ \frac{1}{2} x^2 - x_0 x \right]_x^{x_2} \]

\[ = k \left[ \frac{1}{2} (x_2^2 - x_i^2) - x_0 (x_2 - x_i) \right] \]

\[ = k \left[ \frac{(x_2 - x_i)(x_2 + x_i)}{2} - x_0 (x_2 - x_i) \right] \]

\[ = k (x_2 - x_i) \left[ \frac{x_2 + x_i}{2} - x_0 \right] \]
Similarly: \( P \Delta V \)

Instead of force \( \times \) displacement in one direction,
we have  pressure \( \times \Delta \)Volume
\( \text{(Force/area)} \)

\[
\Delta W = -\int_{V_i}^{V_f} P_{op} \, dV
\]

\( P_{op} \) = opposing pressure

Why negative?
Compression = decrease in volume = work done on system\( \text{ (—)} \)

If \( P \propto \text{constant} \), the integral is easy.

\[
\Delta W = -P_{op} (V_f - V_i) \quad \Rightarrow \quad \text{Work done on the system}
\]

\( \text{at constant pressure} \)
\( \text{(to simplify integral)} \)

Check: compression \( \Rightarrow \) \( V_f < V_i \)
\( \therefore \) \( \Delta W \) = positive

Exercise:
Work through the examples.
Gravity, electrical, friction—
Heat - Xfer of energy

\[ \text{System} \]

\[ T = 20K \quad T = 50K \]

Heat/energy

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 \[ \rightarrow \] Heat capacity of the system

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

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

\[ H = E + \frac{PV}{\text{state variables}} \]

EQUATIONS OF STATE

Examples $PV = nRT$ ← all are state variables (or constants)

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