Variables of State:

e.g. $E = \text{internal energy} \iff \text{describes a state}$

also $P, V, T, n, m (\text{mass})$

Not variables of state:

Heat = $q$ describe a specific way to
Work = $w$ change $E$. Can get to
from $E_1$ to $E_2$ through all
heat, all work, or any
Combination.

Define a NEW variable of state:

Enthalpy $H = E + PV$ formed from a combination
of state variables

Two classes:

Extensive $\Rightarrow$ proportional to mass of the system
\hspace{1cm} e.g. $V, E, H, C$

Intensive $\Rightarrow$ independent of mass of the system
\hspace{1cm} e.g. $P, T, \text{molar heat capacity}, \text{specific heat}$
HEAT AND WORK — TRANSFERS OF ENERGY

\[ \text{Change in energy} \Rightarrow E_2 - E_1 = q + w \]

\[ \text{Energy of final state} \quad \text{energy of initial state} \quad \text{heat transferred to the system} \quad \text{work done on the system (heat flows to)} \]

ASIDE: A CLOSED SYSTEM

This applies for

energies, but not matter

(can be exchanged with surroundings).

This is the first law

\[ \text{(and } E_1 \text{ and } E_2) \]

The important point here is that \( E \) is a state variable; \( q \) and \( w \) are NOT

You can raise the energy of the system by:

1) transferring \( E \) as heat only
2) transferring \( E \) as work only
3) transferring some of each

Can unfold a protein by heating \((T\text{-jump})\)

Can unfold a protein by increasing pressure \((P\text{-jump})\)

Either way puts energy into the system, raising the energy of the protein.
Aside: note that some texts (the minority) define work in an opposite sense, so that \( E = q + w \) \( \neq \) WE WILL NOT

**Reversible Path**

There are many ways of getting from one state (e.g. \( E_1 \)) to another (e.g. \( E_2 \)).

For example:

\[ P_{ex} + \sum P_i = 2 \text{ atm} \]

REVERSIBLE in the limit of infinitely small (large number) of weights.
A reversible path is one in which the process can be reversed at any point along the transition (path).

Simpler example:

At 100°C and 1 atm, the phase transition is poised between liquid and gaseous water (steam)

\[
\begin{align*}
1 \text{ mol } H_2O(\ell) \\
T = 298K \\
P = 1 \text{ atm}
\end{align*}
\rightarrow
\begin{align*}
1 \text{ mol } H_2O(g) \\
T = 273K \\
P = 1 \text{ atm}
\end{align*}
\rightarrow
\begin{align*}
1 \text{ mol } H_2O(g) \\
T = 298K \\
P = 1 \text{ atm}
\end{align*}
\rightarrow
\begin{align*}
1 \text{ mol } H_2O(g) \\
T = 373K \\
P = 1 \text{ atm}
\end{align*}

Constant \( P = \text{ isobaric} \)  \\
Constant \( T = \text{ isothermal} \)

Processes 1 and 2 are easily imagined. Process 3 less so

Processes 1, 2, and 3 are reversible.
Process 4 is not.
We may be interested in the energetics of A → D, but we cannot conduct the measurement.

But if we get from A → → → D by other measurable paths, then the net energetics that we measure provide the original measure we sought.

This is only true iff we are measuring a STATE VARIABLE of the system.

Effects of Changes in T and P

Why do we care?
We know that proteins (and DNA) denature at high temperature.

1) Cooking an egg (protein denatures)
2) PCR — reversible denaturation of DNA (but not the protein!)

Extremophiles ⇒ organisms that grow (and have stable proteins) at high T and P.

We want to know how!?
p. 33 (Table 2.2)

Compares properties of liquid, solid, gaseous water.

Aside: Water has unique properties which dictate most biological interactions. Life evolved in any other solvent would be very different!

Back to heat capacities →

\[ q_p = \int_{273}^{373} C_p \, dT \]

\[ C_p = (1 \text{ mol}) \times (75.4 \text{ J K}^{-1} \text{ mol}^{-1}) = 75.4 \text{ J K}^{-1} \]

\[ \approx \text{constant over range at } 1 \text{ atm} \]

\[ q_p = (75.4 \text{ J K}^{-1}) [373 - 273] K = 7540 \text{ J} \]

What about \( w_p \)?

\[ w_p = \sum P dV = (\text{atm})(\text{Joule}) \]

-volume

\[ \text{Volume} = \frac{\text{mass}}{\text{density}} = \frac{(\text{MW})(\text{moles})}{\text{density}} = (\text{atm})(V_2 - V_1) \]

\[ V_2 - V_1 = (\text{MW})(\text{mol}) \left[ \frac{1}{P_{\text{H}_{2}O}} - \frac{1}{P_0} \right] \]

\[ = (18 \text{ g mol}^{-1})(1 \text{ mol}) \left[ \frac{1}{0.9984} - \frac{1}{0.9999} \right] \text{g cm}^{-3} \]

\[ = 0.78 \text{ cm}^3 \]

- \((1.0434 - 1.6000)\)
\[
W_p = (1 \text{ atm} \times 0.78 \text{ cm}^3) \left[0.1013 \frac{\text{J}}{\text{cm}^3 \cdot \text{atm}}\right] \\
= 0.079 \text{ J}
\]

Contrast this with \( q_p = 7540 \text{ J} \)

i.e. all the change in \( E \) is from \( q_p \)

\[E_2 - E_1 = q_p + W_p = 7540 \text{ J} = \Delta E\]

Similarly,

\[H_2 - H_1 = E_2 + P_2 V_2 - E_1 - P_1 V_1\]

\[H = E + PV\]

\[= E_2 - E_1 - (P)(V_2 - V_1)\]

\[\Delta H = 7540 \text{ J} \quad \text{(actually, exactly)}\]

Why?

\[\underline{PV \ Work \ and \ Gas \ Expansion}\]

Irreversible

\[W = - \int P \text{d}V \quad P = P_{ex} = \text{const.}\]

\[= -P(V_2 - V_1)\]
Reversible, isothermal

\[ \omega = - \int P \text{d}V \]

Pressure slowly changes, temperature constant

From ideal gas law \( P = \frac{nRT}{V} \)

\[ \omega_r = - \int \frac{nRT}{V} \text{d}V \text{ but } n, R, \text{ and } T \text{ constant} \]

\[ = -nRT \int \frac{V_2}{V} \frac{\text{d}V}{V} \]

\[ = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_2}{P_1} \]

Why “sub-T”?

So work irreversible \( \Rightarrow -P(V_2 - V_1) \)

work reversible \( \Rightarrow -nRT \ln \frac{V_2}{V_1} \)

---

For an ideal gas (no inter-molecule interactions),

\( E \) should be independent of pressure

\[ S_0 \]

\[ E_2 - E_1 = 0 = q_T + \omega_r \]

\[ \text{temperature constant} \]

\[ \therefore q_T = -\omega_r = -nRT \ln \frac{V_2}{V_1} \]