Variables of State:

e.g. E = internal energy ⇐ describes a state
also P, V, T, n, m (mass)

Not variables of state:

Heat = q
Work = w

describe a specific way to change E. Can get 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

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Two classes:

Extensive ⇒ proportional to mass of the system
e.g. V, E, H, C

Intensive ⇒ independent of mass of the system
e.g. P, T, molar heat capacity, specific heat

HEAT AND WORK — TRANSFERS OF ENERGY

Change in energy $\Rightarrow$ $E_2 - E_1 = q + w$

- E_2: energy of final state
- E_1: energy of initial state
- q: heat transfered to the system (heat flows to)
- w: work done on the system (work to)

ASIDE: THIS APPLIES FOR A CLOSED SYSTEM (energy, but not matter can be exchanged with surroundings).

THIS IS THE FIRST LAW

The important point here is that E (and E_1 and E_2) is a state variable, q and w are NOT

You can raise the energy of the system by:

1) transfering E as heat only
2) transfering E as work only
3) transfering some of each

Can unfold a protein by heating (T-jump)

Can unfold a protein by increasing pressure (P-jump)

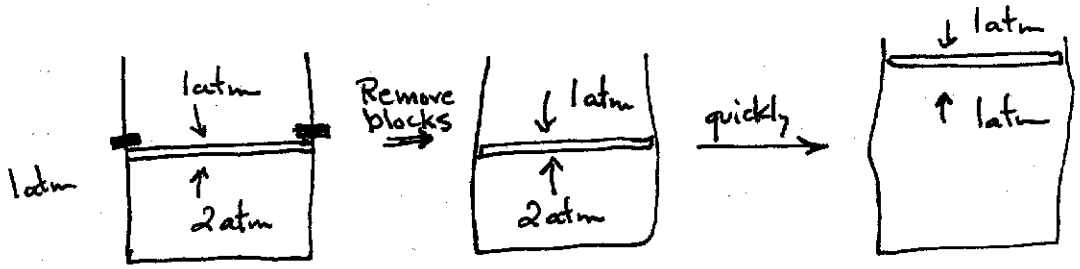
Either way puts energy into the system, raising the energy of the protein

Aside: note that some texts (the minority) define work in an opposite sense, so that $E = q - w$ ⇐ WE WILL NOT

Reversible Path

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

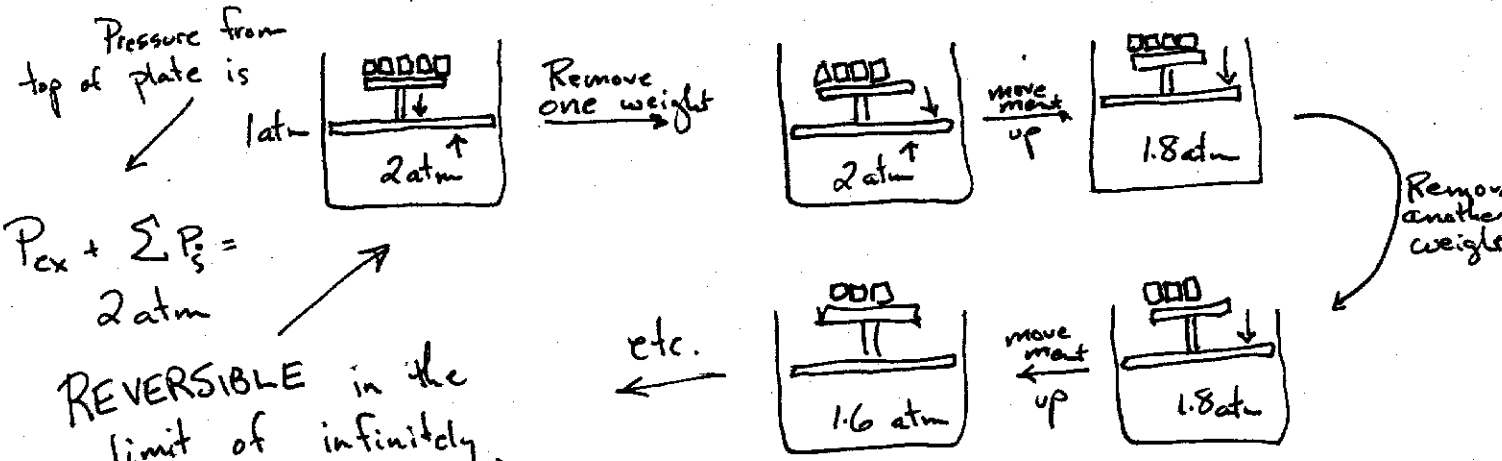
e.g.



IRREVERSIBLE expansion → after blocks are removed pressure difference drives rapid movement of the piston. Pressure on two sides of piston plate not equal.

Pressure from top of plate is

$P_{ex} + \sum P_s =$ 2 atm

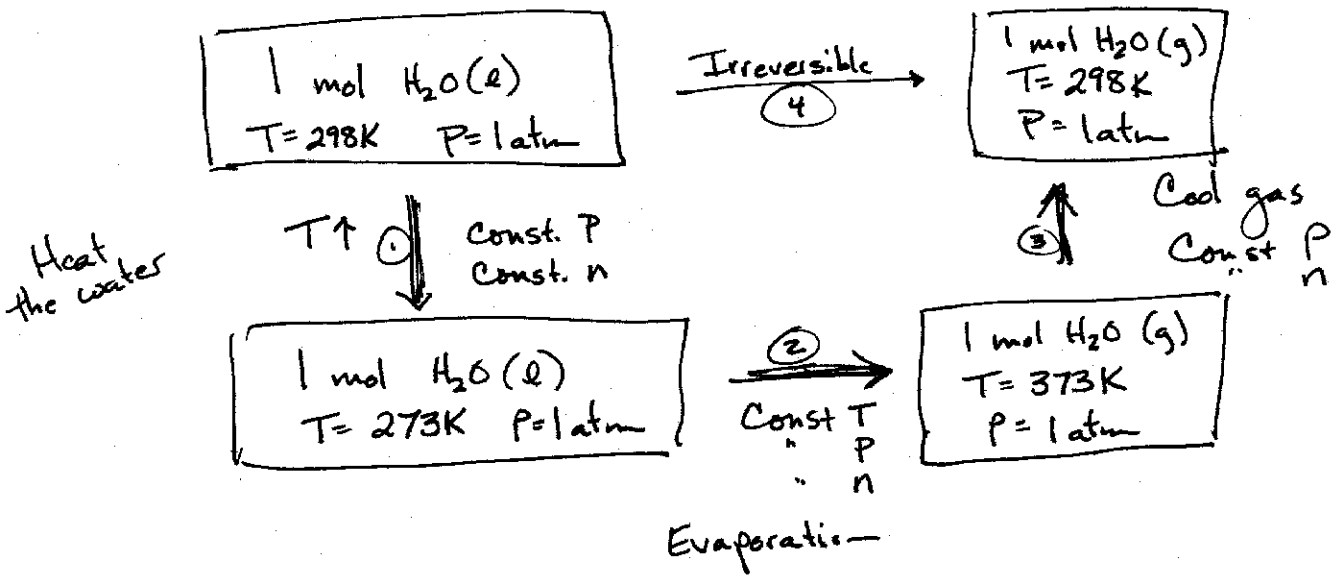


REVERSIBLE in the limit of infinitely small (large number) of weights

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)



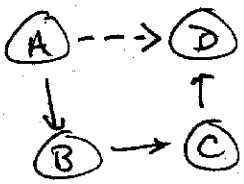
Constant P = isobaric
Constant T = isothermal

Constant volume = isochoric
No heat xferred ($q=0$) = adiabatic
↑ isolated system

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

Processes (1), (2), and (3) are reversible
Process (4) is not.

Why construct these paths?



Measurement is often easier along reversible paths

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

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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!?

Overhead?

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 →

Heat 1 mol water from 0°C → 100°C (l → l) [1 atm]

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

Constant pressure

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

≈ constant over range at 1 atm

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

What about w_p? $\quad w_p = \int P\,dV = (1\ \text{atm}) \int_{V_1}^{V_2} dV$

$$= (1\ \text{atm})(V_2 - V_1)$$

$$\text{Volume} = \frac{\text{mass}}{\text{density}} = \frac{(\text{MW})(\text{moles})}{\text{density}}$$

Look in table 2.2

$$\therefore\ V_2 - V_1 = (\text{MW})(\text{moles})\left[\frac{1}{\rho_{100}} - \frac{1}{\rho_0}\right]$$

$$= (18\ \text{g mol}^{-1})(1\ \text{mol})\left[\frac{1}{0.9584} - \frac{1}{0.9999}\right] \text{g}^{-1}\,\text{cm}^3$$

$$= 0.78\ \text{cm}^3 \qquad (1.0434 - 1.0000)$$

Do for homework

$$w_p = (1\,atm)(0.78\,cm^3)\left[0.1013\,\frac{J}{cm^3 \cdot atm}\right]$$

$$= 0.079\ J$$

Contrast this with $q_p = 7540\,J$

i.e. all the change in E is from q_p

$$\therefore \quad E_2 - E_1 = q_p + w_p = 7540\,J = \Delta E$$

Similarly,

$$H_2 - H_1 = E_2 + P_2V_2 - E_1 - P_1V_1$$

$H = E + PV$

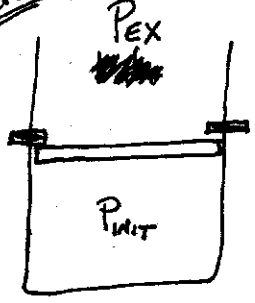
$$= E_2 - E_1 - (P)(V_2 - V_1)$$

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

Why?

PV Work and Gas Expansion

Irreversible



$$w = -\int P\,dV \qquad P = P_{ex} = \text{const}$$

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

Reversible, isothermal

$$w = -\int P_{ex}\, dV$$

Pressure slowly changes, temperature constant

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

$$w_T = -\int \frac{nRT}{V}\, dV \qquad \text{but } n, R, \text{ and } T \text{ constant}$$

why "sub-T?"

$$= -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

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

WHY?

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

work reversible $\rightarrow -nRT \ln V_2/V_1$

FOR AN IDEAL GAS (no inter-molecule interactions), E should be independent of pressure

So $E_2 - E_1 = 0 = q_T + w_T$

temperature constant
Pressure irrelevant

$$\therefore q_T = -w_T = +nRT \ln V_2/V_1$$