B.Sc. (Honours) Part-I

Paper-I

Topic: Understanding of Law of Thermodynamics

UG

Subject-Chemistry

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Understanding of Law of Thermodynamics

A *thermodynamic system* is a collection of objects we can regard as a unit, that can exchange energy with its surroundings.

We can now think about energy transfers into and out of these systems; through

– heat transfer Q and

– work W

Sign convention

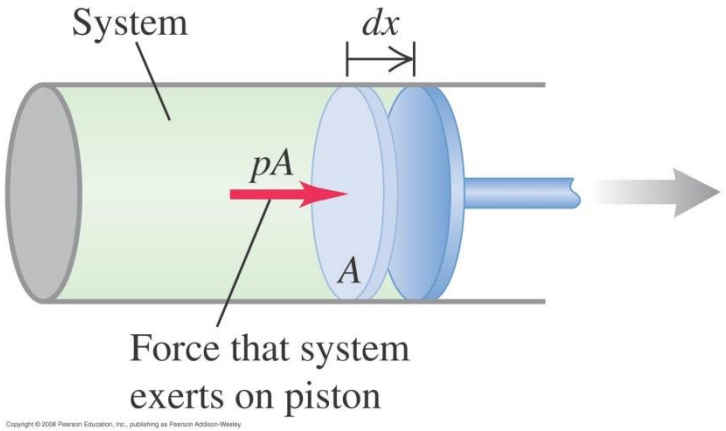
We need to be careful about signs:

Q_{in} is positive
Q_{out} is negative

W done *by* the system is positive
W done *on* the system is negative

Let's look at work done during volume changes.

Pressure exerts a force on the piston, which moves from x_1 to x_2:



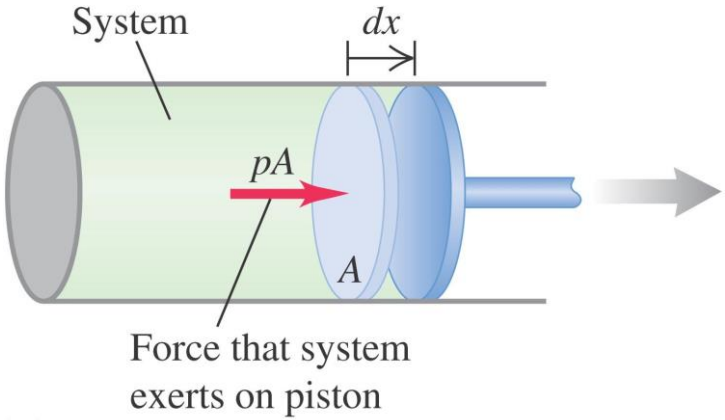
$$W = \int_{x_1}^{x_2} F \cdot dx = \int_{x_1}^{x_2} (pA)\,dx$$

$$= \int_{V_1}^{V_2} p\,dV$$

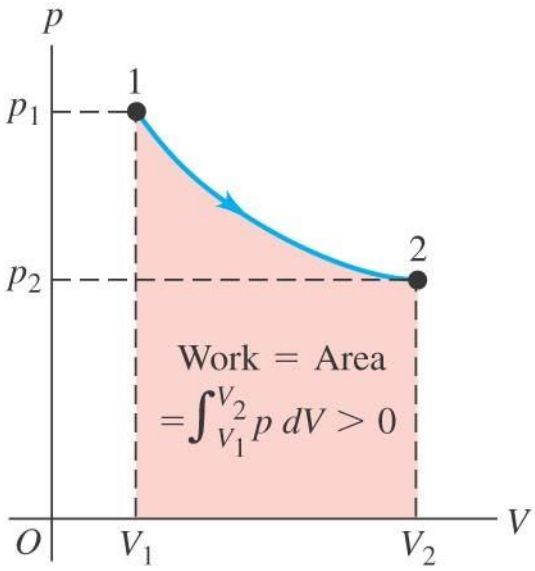
$W > 0$ energy removed from system (work is done by the system against its surroundings) (expansion)

$W < 0$ energy added to system (work is done on the system) (compression)

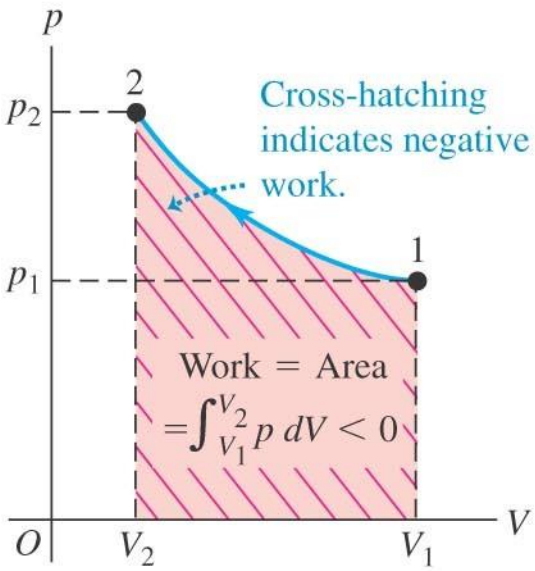
So the *work done* equals the *area* under a *pV* curve.



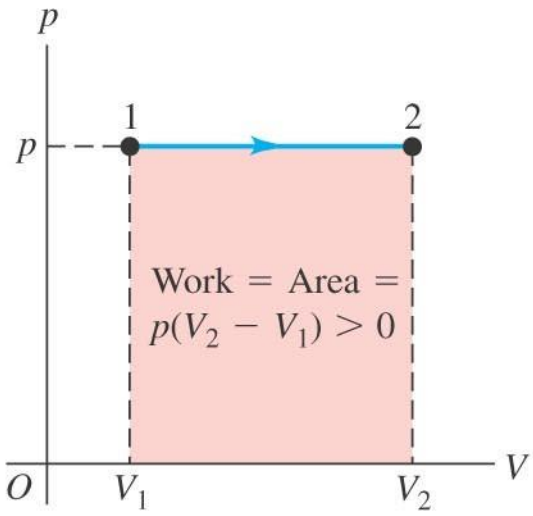
(a) *pV*-diagram for a system undergoing an expansion with varying pressure



(b) *pV*-diagram for a system undergoing a compression with varying pressure



(c) *pV*-diagram for a system undergoing an expansion with constant pressure



There can be many different paths from one thermodynamic state to another, so the work done by a system during a transition between two states depends on the path chosen