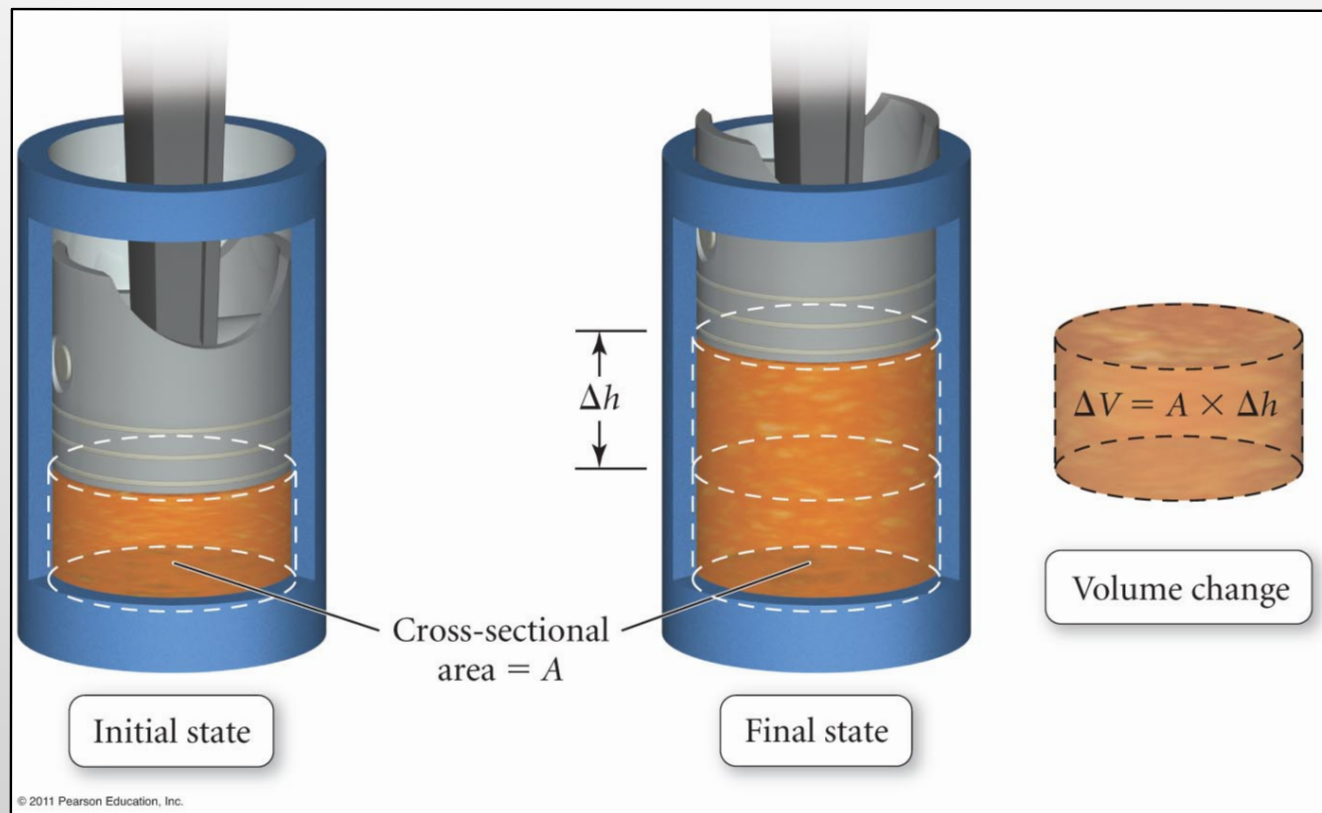


## Pressure –Volume Work: *Moving of a Piston against External Pressure*



$$w = F \cdot D$$

$$P = F / A \quad \text{or} \quad F = P \cdot A$$

$$\Rightarrow w = P \cdot A \cdot D$$

$$w = P \cdot A \cdot \Delta h$$

$$w = P \cdot \Delta V$$

The system is “doing” work, i.e.,  $w$  must be negative

$$w = - P \cdot \Delta V$$

What is the work when a balloon is expanded from 0.1L to 1.85L against a pressure of 1 atm?

Find  $P, \Delta V \Rightarrow w$

$$P = 1 \text{ atm} \cdot \frac{101325 \text{ Pa}}{1 \text{ atm}} = 101325 \text{ Pa}$$

$$1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$$

$$\Delta V = V_f - V_i = 1.85 \text{ L} - 0.100 \text{ L} = 1.75 \text{ L} = 1 \text{ dm}^3$$

$$1 \text{ L} \hat{=} \text{dm}^3 = 1 \text{ dm}^3 \cdot \frac{1 \text{ m}^3}{1000 \text{ dm}^3} = 1.75 \cdot 10^{-3} \text{ m}^3$$

$$w = -P \Delta V = -101325 \text{ Pa} \cdot 1.75 \cdot 10^{-3} \text{ m}^3$$

$\text{kg m}^{-1} \text{ s}^{-2}$

$$w = -177 \text{ kg m}^2 \text{ s}^{-2} = -177 \text{ J}$$

### Example: Total energy change

A chemical reaction between two gases releases 110 kJ. The work that is done on the surroundings is 1700 J. Calculate  $\Delta E$ . Is the reaction endo- or exothermic?

$$\Delta E = q + w$$

$$q = -110 \text{ kJ} \cdot \frac{1000 \text{ J}}{1 \text{ kJ}} = -110000 \text{ J}$$

$$w = -1700 \text{ J}$$

$$\begin{aligned} \Delta E &= -110000 \text{ J} + (-1700 \text{ J}) = -111700 \text{ J} \\ &= -112 \text{ kJ} \end{aligned}$$

Enthalpy  $H$  of a system is the sum of internal energy and product of pressure and volume

$$H = E + PV$$

$$\Delta H = \Delta E + P\Delta V \quad (\text{at constant pressure})$$

$$\text{Since } \Delta E = q + w$$

$$\Delta E = q_p + w \quad (\text{at const. pressure})$$

$$w = -P\Delta V \Leftrightarrow P\Delta V = -w$$

$$\Delta H = (q_p + w) - w$$

$$\Delta H = q_p$$

What is the difference between  $\Delta E$  and  $\Delta H$ ?

$\Delta E$  is the measure of all energy exchanged with the surroundings (heat and work)

$\Delta H$  measure of heat exchanged with the surroundings at constant pressure

State whether  $\Delta H$  is less than, equal to or larger than  $\Delta E$

a). an ideal gas is cooled at constant pressure

$$\Delta H = \Delta E + P\Delta V \quad P\Delta V \text{ negative b/c}$$
$$\Delta H < \Delta E \quad \text{volume decreases}$$

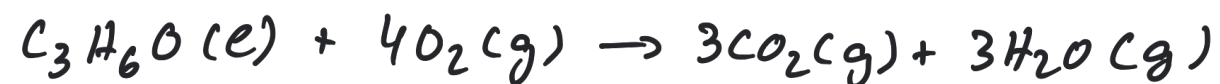
b). a mixture of gases undergoes an exothermic reaction in a container of fixed volume

$$\Delta H = \Delta E \quad \text{b/c } \Delta V = 0$$

c). a solid yields a mixture of gases in an exothermic reaction that takes place in a container of variable volume

$$\Delta H > \Delta E \quad \text{b/c volume increases}$$

The combustion of acetone has the following chemical reaction:



$$\Delta H_{\text{rxn}}^{\circ} = -1790 \text{ kJ/mol}$$

standard conditions  
273.15 K  
100 kPa / 1 bar

$$V = 177 \text{ mL} ; d = 0.788 \text{ g/mL}$$

How much heat is released by its complete combustion?

Concept:

Volume  $\rightarrow$  mass  $\rightarrow$  moles  $\rightarrow$   $q_p$

$$\text{mass} = 177 \text{ mL} \cdot \frac{0.788 \text{ g}}{1 \text{ mL}} = 139.5 \text{ g}$$

$$M_w = 58.08 \text{ g/mol}$$

$$\text{moles} = 139.5 \text{ g} \cdot \frac{1 \text{ mol}}{58.08 \text{ g}} = 2.40 \text{ mol}$$

$$\begin{aligned} q_p = \Delta H &= n \cdot \Delta H_{\text{rxn}}^{\circ} = 2.40 \text{ mol} \cdot (-1790 \text{ kJ/mol}) \\ &= -4296 \text{ kJ} \end{aligned}$$