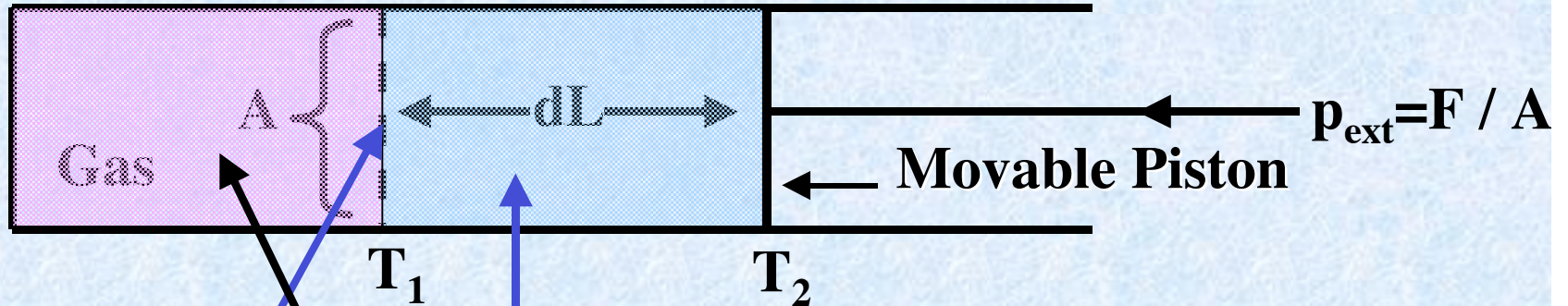


**Bonus \* Bonus \* Bonus**

**Definition of work using calculus:**

**Infinitesimal work done  $dw$  by infinitesimal change in volume of gas  $dV$ :**



$$\text{work} = dw = F \cdot dL = (A p_{\text{ext}}) \cdot dL = p_{\text{ext}} \cdot (A dL)$$

But,  $A dL = V_2 - V_1 = dV$  (infinitesimal volume change)

$$dw = p_{\text{ext}}(V_2 - V_1) = p_{\text{ext}} dV \quad \text{But sign is arbitrary, so choose } \square$$

$$dw = -p_{\text{ext}} dV \quad (w < 0 \text{ is work done by gas, } dV > 0)$$

$$\boxed{dw = -p_{\text{ext}} dV}$$

(Note!  $p$  is the **external** pressure on the gas!)

$$dw = - p_{\text{ext}} dV$$

Total work done in any change is the sum of little infinitesimal increments for an infinitesimal change  $dV$ .

$$\int dw = \int - p_{\text{ext}} dV = w \text{ (work done by the system )}$$

Two Examples :

( 1 ) pressure = constant =  $p_{\text{external}}$ ,

$V$  changes  $v_i \rightarrow v_f$

$$w = \int_{v_i}^{v_f} p_{\text{ext}} dV = - p_{\text{ext}} \int_{v_i}^{v_f} dV = - p_{\text{ext}} ( v_f - v_i ) = - p_{\text{ext}} \Delta V \quad \square$$

{ Irreversible expansion if  $p_{\text{ext}} \neq p_{\text{gas}}$

That is if,  $p_{\text{gas}} = nRT/V \neq p_{\text{external}}$  }

Example 2 :  $dV \neq 0$ , but  $p \neq \text{const}$  and  $T = \text{const}$ :

$$p_{\text{ext}} = p_{\text{gas}} = \frac{nRT}{V} \quad (\text{Called a } \textit{reversible} \text{ process.})$$

$$w = - \int nRT \frac{dV}{V}$$

$$w = - \int_{V_i}^{V_f} nRT \frac{dV}{V} = - nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

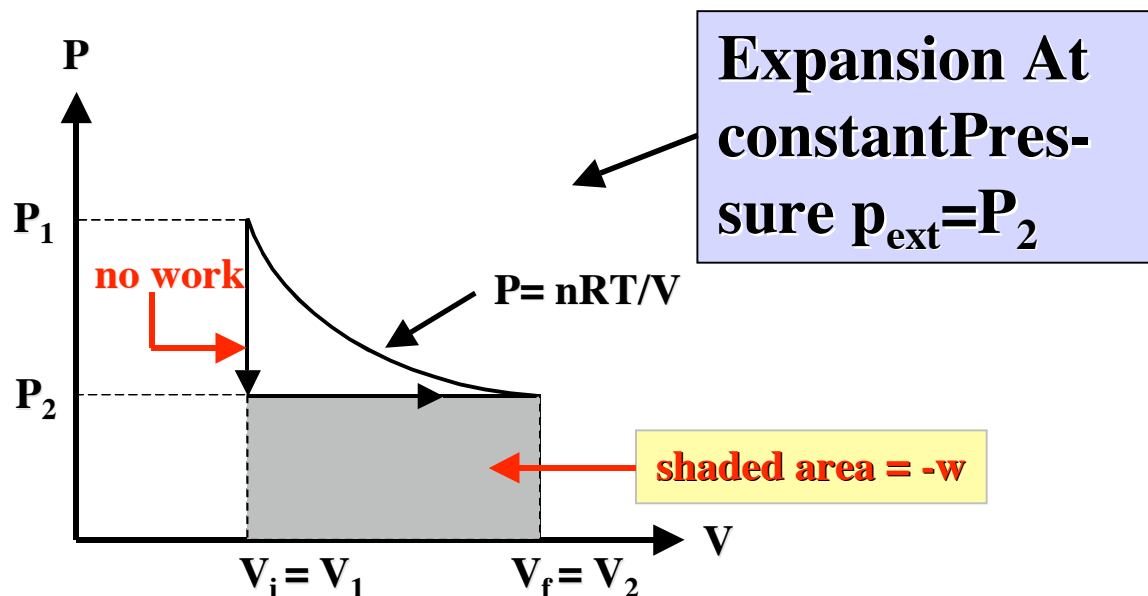
$$w = - nRT \ln ( V_f / V_i )$$

[Remembering that  $\int f(x) dx$  is the area under  $f(x)$  in a plot of  $f(x)$  vs  $x$ ,  
 $w = - \int pdV$  is the area under  $p$  in a plot of  $p$  vs  $V$ .]

$P, V$  not const but  $PV = nRT = \text{const}$  (Isothermal change)

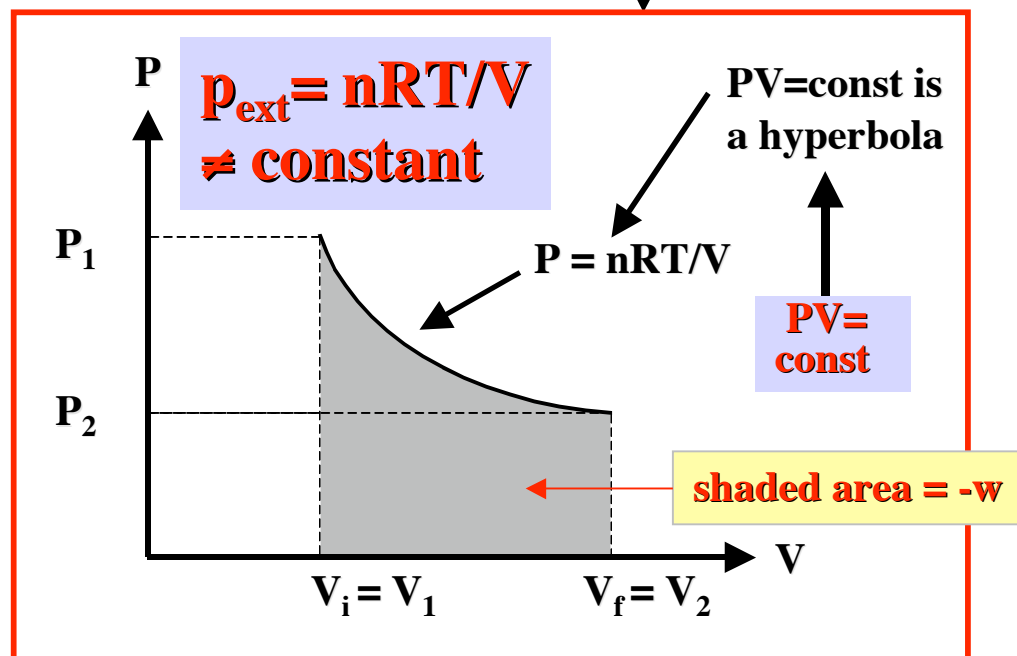
{ **Reversible isothermal expansion because**  $p_{\text{ext}} = p_{\text{gas}}$  }

# Graphical representation of $\int p_{\text{ext}} dV$



**Isothermal reversible expansion**

Compare the shaded area in the plot above to the shaded area in the plot for a reversible isothermal expansion with  $p_{\text{ext}} = p_{\text{gas}} = nRT/V$



**Work done is NOT independent of path : Change the State of a gas two different ways:**

Consider n moles of an ideal gas

Initial condition:  $T_i = 300 \text{ K}$ ,  $V_i = 2 \text{ liter}$ ,  $p_i = 2 \text{ atm}$ .

Final condition:  $T_f = 300 \text{ K}$ ,  $V_f = 1 \text{ liter}$ ,  $p_f = 4 \text{ atm}$ .

Path 1 consists of two steps:

Step 1 : 2 atm, 2 l, 300K  $\xrightarrow[\text{compress}]{\text{cool at const p}}$  2 atm, 1 l, 150K

$\Delta V \neq 0$  for this step

Step 2: Warm at constant V: 2 atm, 1 liter, 150 K  $\rightarrow$  4 atm, 1 liter, 300 K.

$\Delta V = 0$  for this step

$w = - p_{\text{ext}} ( V_f - V_i )$  for the first step,  $p_{\text{ext}} = \text{const} = 2 \text{ atm}$

$w = - 2 \text{ atm} ( 1 - 2 ) l = 2 l \text{-atm}$

$w = 0$  for 2nd step since  $V = \text{const}$

**$w_{\text{tot}} = 2 l \text{-atm}$**

**Path 2 is a single step reversible isothermal compression:**

**2 atm, 2 l, 300K  $\rightarrow$  4 atm, 1 l, 300K (T constant)**

$$P_{\text{ext}} = P_{\text{gas}} = nRT/V = p$$

$$w = - \int_{v_i}^{v_f} p \, dV = - \int_{v_i}^{v_f} nRT \frac{dV}{V} = - nRT \int_{v_i}^{v_f} \frac{dV}{V}$$

$$w = - nRT \ln ( v_f / v_i ) = -nRT \ln ( 1/2 )$$

Since  $nRT = \text{const} = PV = 4 \text{ l-atm}$

$$w = -4 \text{ l-atm} ( \ln 1/2 ) = ( .693 ) 4 \text{ l-atm} = 2.772 \text{ l-atm}$$

Compare to  $w$  for path 1:  $w = 2 \text{ l-atm}$

**$w$  for two different paths between same initial and final states is NOT the same. Work is NOT a state Function!**

**Heat : Just as work is a form of energy, heat is also a form of energy.**

**Heat is energy which can flow between bodies that are in thermal contact.**

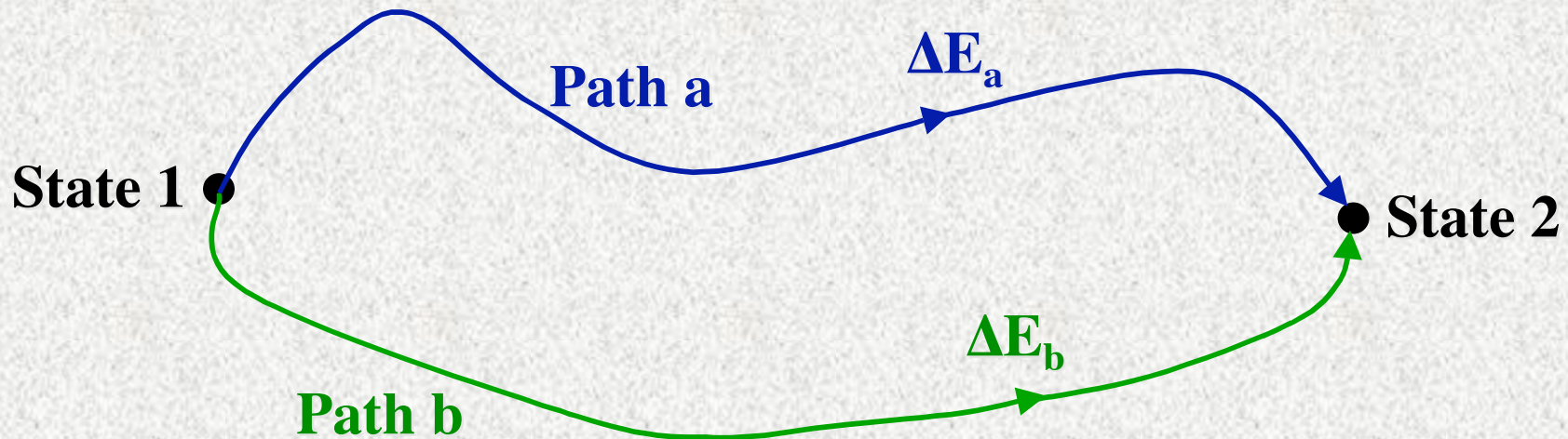
**In general heat can be converted to work and work to heat -- can exchange the various energy forms.**

**Heat is also NOT a state function. The heat change occurring when a system changes state very definitely depends on the path.**

**Can prove by doing experiments, or (for ideal gases) can use heat capacities to determine heat changes by different paths.**

# The First Law of Thermodynamics

I) Energy is a state function for any system :



$\Delta E_a$  and  $\Delta E_b$  are both for going from 1  $\rightarrow$  2

If E not a state function then:  $\Delta E_a \neq \Delta E_b$

Suppose  $\Delta E_a > \Delta E_b$  - now go from state 1 to state 2 along path a, then return to 1 along path b.



Energy change =  $\Delta E = E_a - E_b$

$\Delta E > 0$ . Have returned system to its original state and created energy.

Experimentally find no situation in which energy is created, therefore,  $E_a = E_b$  and energy is a state function.  
No one has made a perpetual motion machine of 1st kind.

## The First Law

**The energy increase of a system in going between two states equals the heat added to the system plus the work done on the system.**

$\Delta E = q + w$  (Here is where choice of sign for  $w$  is made)

$$dE = dq + dw$$

$q > 0$  for heat added to the system

$w > 0$  for work done on the system ( $dV < 0$ )

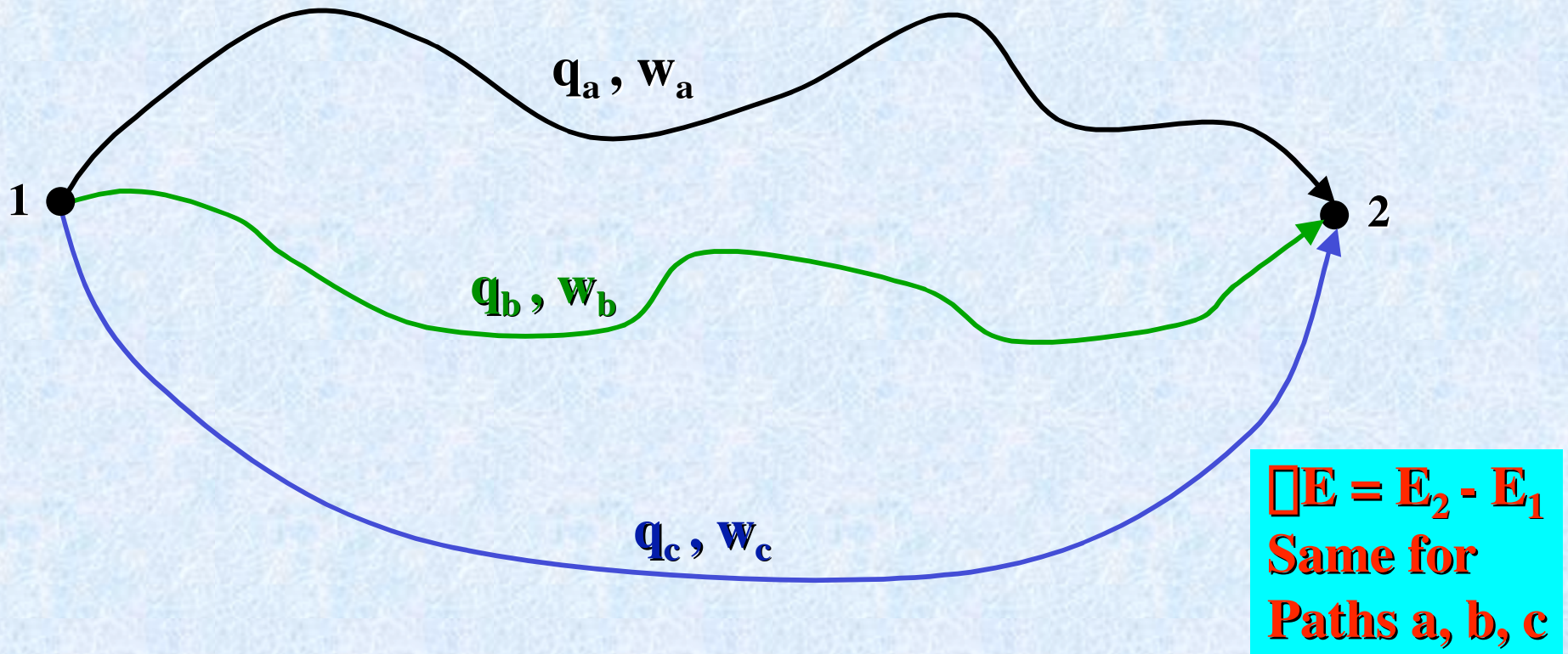
$dw = -p_{\text{ext}}dV$  ( $w < 0$  is work done by system,  $dV > 0$ )

Totally empirical law. The result of observations in many, many experiments.

$\Delta E$  is a state function independent of the path.

$q$  and  $w$  are NOT state functions and do depend on the path used to effect the change between the two states of the system.

**Taking a system over different paths results in  
same  $\Delta E$  but different  $q, w$ :**



$q_a, q_b, q_c$  all different,  $w_a, w_b, w_c$  all different, but

$$q_a + w_a = q_b + w_b = q_c + w_c = \Delta E = E_2 - E_1$$

## Measurements of $\Delta E$

Suppose we want to measure  $\Delta E$  for the following change :

**Initial State and system:  $O_2$  and  $N_2$  gas at  $25^\circ C$  and  $P(O_2) = P(N_2) = 1 \text{ atm.}$  (1 mole each)**

**Final State : 2 moles  $NO$  at  $25^\circ C$ , 1 atm.**

**(This is really a conversion of energy stored in the chemical bonds of  $O_2$  and  $N_2$  into stored chemical energy in the  $NO$  bond.)**

We know  $\Delta E = q + w$

a) What is  $w$ ? 1st let us carry the change above out at constant volume :



Then no mechanical work is done by the gases as they react to form NO because they are not coupled to the world --- no force moving through a distance --- nothing moves  $\Delta w = 0$ .

$$\Delta E = q_v$$

**Change in energy for a chemical reaction carried out at constant volume is directly equal to the heat evolved or absorbed.**

If  $q_v > 0$  then  $\Delta E > 0$  and energy or heat is absorbed by the system. This is called an **endoergic reaction**.

If  $q_v < 0$  then  $\Delta E < 0$  and energy or heat is evolved by the system. This is called an **exoergic reaction**.

Can we find or define a new state function which is equal to the heat evolved by a system undergoing a change at constant pressure rather than constant volume?

i.e. is there a state function =  $q_p$ ?

Yes!  $H \equiv E + pV$  will have this property

Note  $E, p, V$  are state fcts.  $\square$   $H$  must also be a state fct.

Let us prove  $\square H = q_p$  : (for changes carried out at constant  $p$ )

$$\square E = q + w \quad \square H = \square E + \square (pV)$$

$$\square H = q_p + w + p \square V, \text{ since } p = \text{const}$$

$$w = -p \square V \text{ for changes at const } p$$

$$\square \square H = q_p - p \square V + p \square V \quad \square \quad \square H = q_p$$

$$dH_p = dq_p + dw + pdV ; dw = -pdV$$

$$dH = dq_p - pdV + pdV = dq_p \quad \square \quad dH = dq_p$$