

Ideal Gas State functions: Consider 1 mole of an ideal gas

$$PV = RT$$

Suppose begin with:

$$P_1 = 5 \text{ atm} \quad V_1 = 4.92 \text{ liters}$$

$$T_1 = 300^\circ \text{ K}$$

And end with:

$$P_2 = 4 \text{ atm} \quad V_2 = 12.3 \text{ liters}$$

$$T_2 = 600^\circ \text{ K}$$

$$\Delta P = 4 - 5 = -1 \text{ atm} \rightarrow \quad \Delta V = 7.38 \text{ liters}$$

$$\Delta T = 600 - 300 = 300^\circ$$

If we got to the condition 4 atm, 12.3 liters,
and 600°K by going as follows:

5 atm, 4.92 liters, 300° → 4 atm, 6.15 liters, 300° → 4 atm,
12.3 liters, 600° or by the path:

5 atm, 4.92 liters, 300° → 5 atm, 9.84 liters, 600° → 4 atm,
12.3 liters, 600°

Would get same $\Delta P, \Delta V, \Delta T$

Changes in state functions are independent of path.

Important State Functions:

T, P, V, Entropy, Energy and any combination of the above.

Important Non State Functions: Work, Heat.

Bonus * Bonus * Bonus

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

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_{external} ,

V changes $v_i \rightarrow v_f$

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

{ 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 $T = \text{const}$:

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

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

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

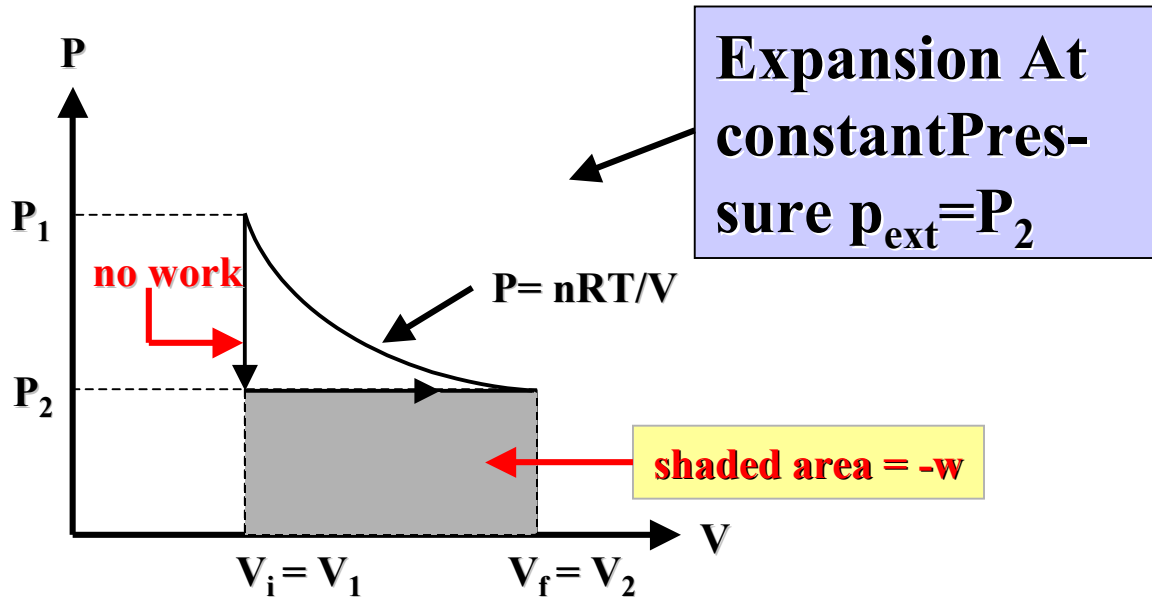
$$w = - nRT \ln (V_f / V_i)$$

[Remembering that $\int f(x) dx$ is the area under $f(x)$ in a plot of $f(x)$ vs x ,
 $w = - \int p dV$ 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 $p_{\text{ext}} = p_{\text{gas}}$ }

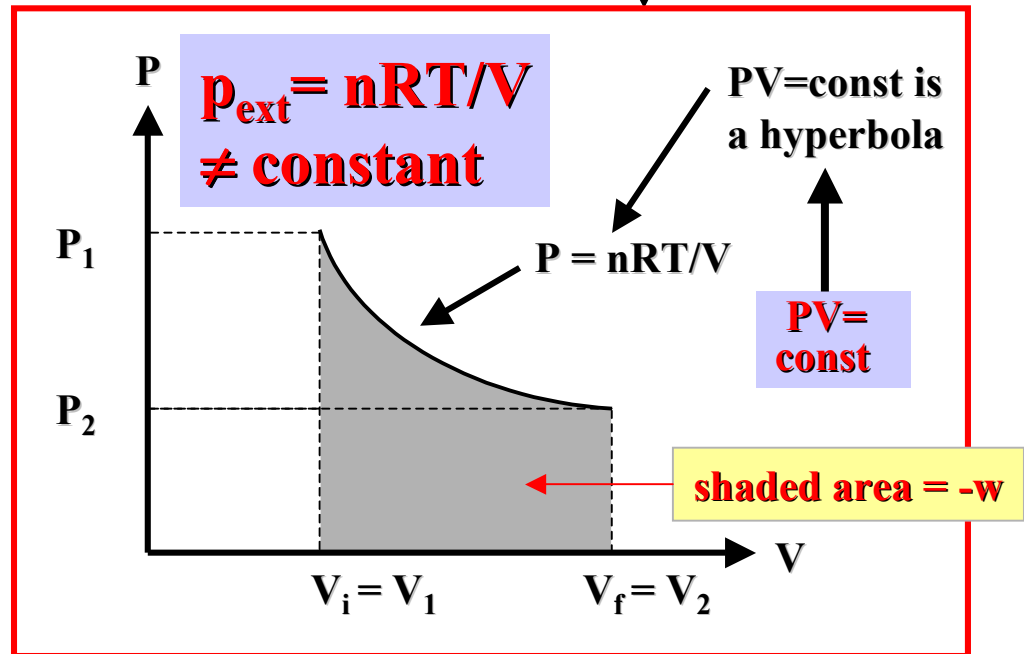
Graphical representation of $\int p_{\text{ext}} dV$



(If done at constant T, gas pressure follows curved $P = nRT/V$ path while p_{ext} remains fixed)

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

$\Delta V \neq 0$ for this step

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

$\Delta V = 0$ for this step

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

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

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

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

Path 2 is a single step reversible isothermal compression:

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

$$\begin{aligned} P_{\text{ext}} &= P_{\text{gas}} \\ nRT/V &= p \end{aligned}$$

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

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

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

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

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.

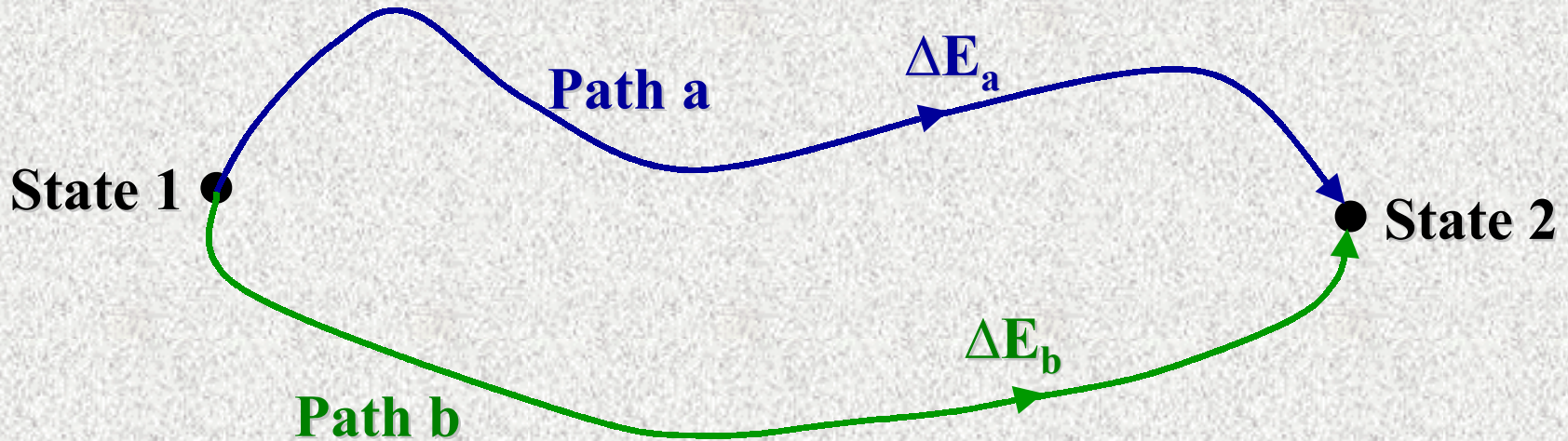
In general heat can be converted to work and work to heat -- can exchange the various energy forms.

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 :



ΔE_a and ΔE_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 = $\Delta E = \Delta E_a - \Delta E_b$

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

Experimentally find no situation in which energy is created, therefore, $\Delta E_a = \Delta E_b$ 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 ($dV < 0$)

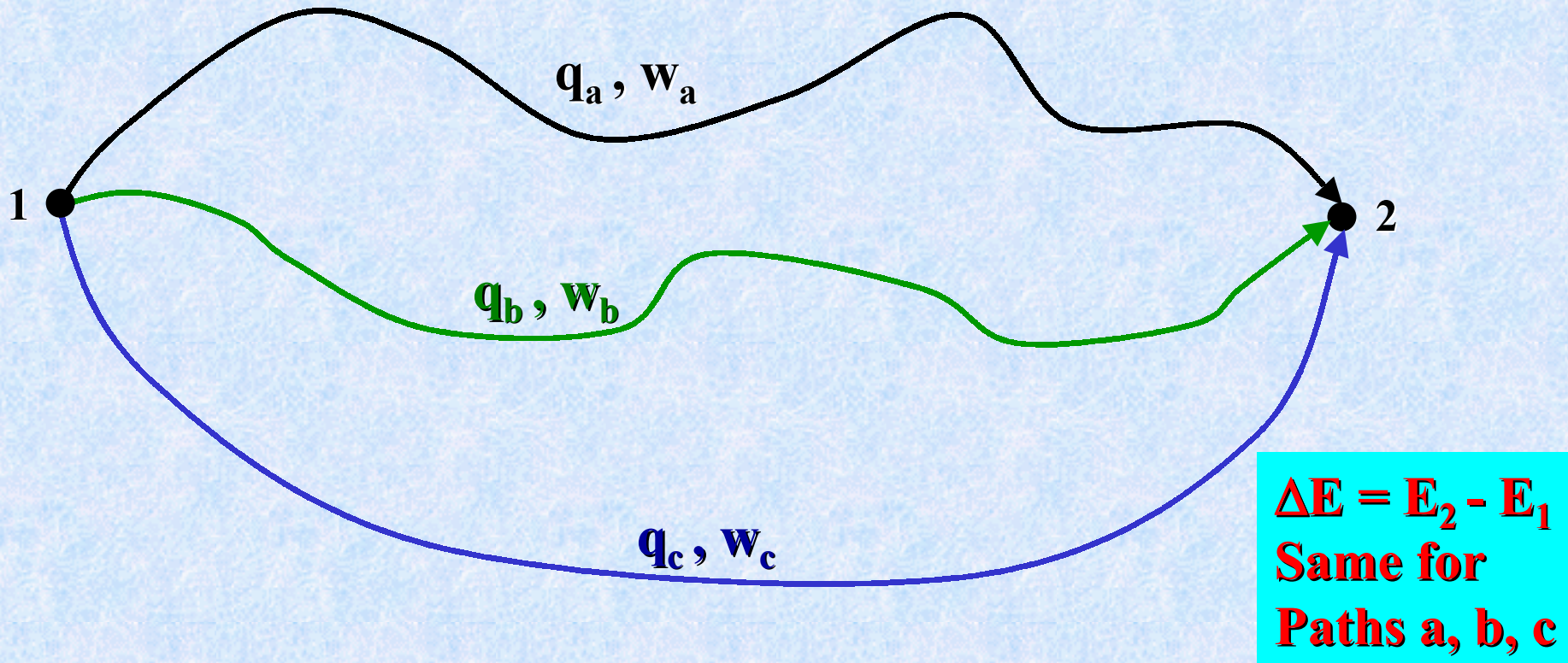
$dw = -p_{\text{ext}} dV$ ($w < 0$ is work done by system, $dV > 0$)

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

ΔE 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 ΔE 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 ΔE

Suppose we want to measure ΔE for the following change :

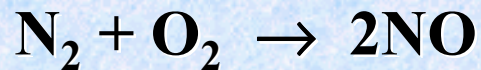
Initial State and system: O_2 and N_2 gas at $25^\circ C$ and $P(O_2) = P(N_2) = 1 \text{ atm.}$ (1 mole each)

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 $\rightarrow w = 0$.

$$\Delta E = q_v$$

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. $\therefore H$ must also be a state fct.

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

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

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

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

$$\therefore \Delta H = q_p - p \Delta V + p \Delta V \rightarrow \Delta H = q_p$$

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

$$dH = dq_p - pdV + pdV = dq_p \rightarrow dH = dq_p$$

H is called the enthalpy. The enthalpy change for a system at constant pressure equals the heat absorbed or released.

Exothermic process $q_p < 0$ heat evolved $\Delta H < 0$

Endothermic process $q_p > 0$ heat absorbed $\Delta H > 0$

Are ΔH and ΔE similar (i.e. are q_v , q_p similar) ?

$$\Delta H = \Delta E + \Delta (pV)$$

Obviously when

$$\Delta (pV) \ll \Delta E$$

$$\Delta H \approx \Delta E$$

For reactions where only liquids and solids are involved, and where reaction is carried out at constant pressure (usually in the presence of the atmosphere) ΔV and therefore $\Delta (pV) = p \Delta V$ is usually negligible.

For gas phase reactions, $\Delta (pV)$ can be large. For a reaction carried out at const T: