

# Work in an Irreversible Isothermal Expansion [T constant]

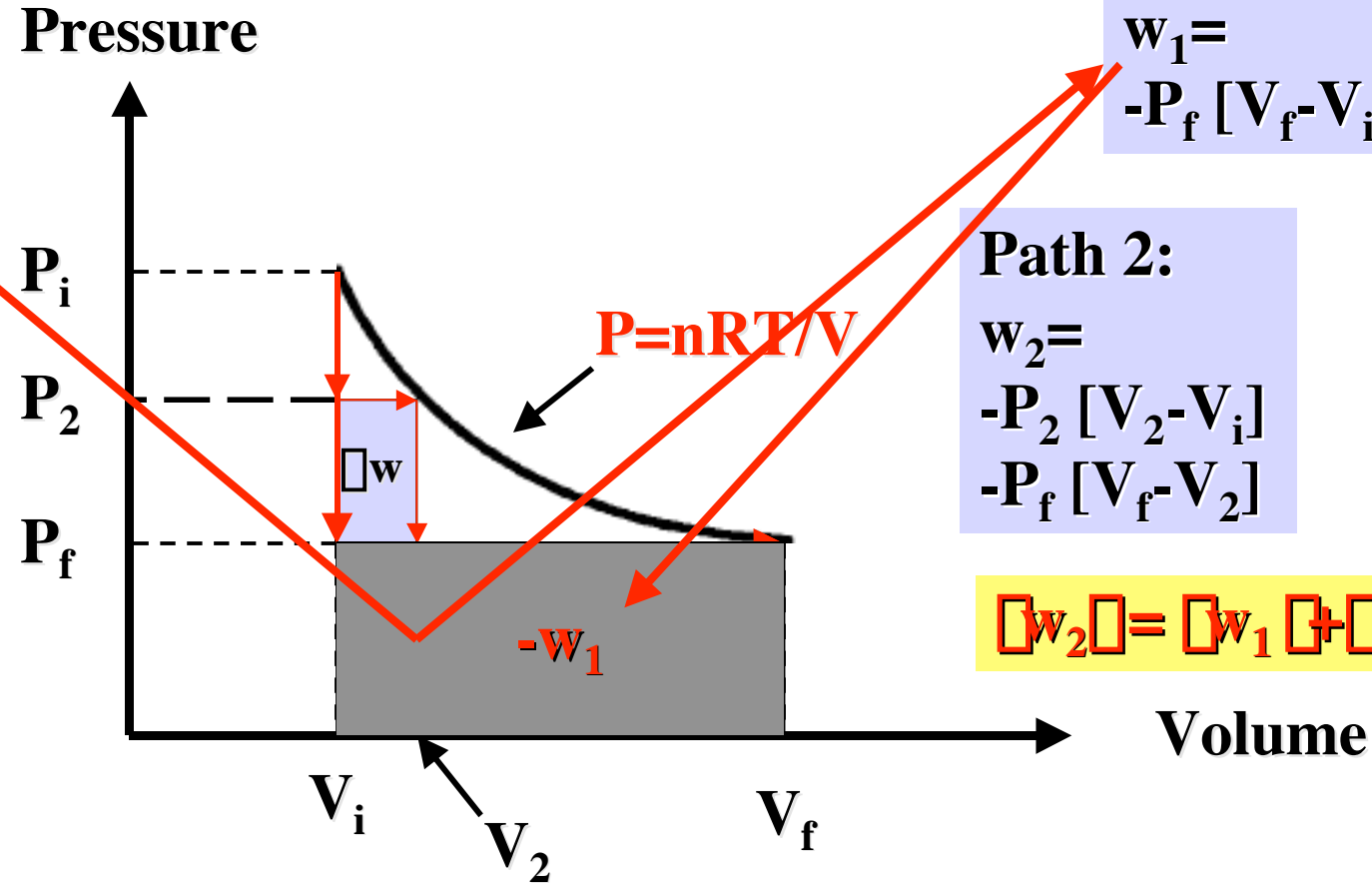
**Path 1:**  
 $P_i \rightarrow P_f$   
 at start  
 with  
 $V_i \rightarrow V_f$

**Path 1:**  
 $w_1 = -P_f [V_f - V_i]$

**Path 2:**  
 $P_i \rightarrow P_2 \rightarrow P_f$   
 stopping at an  
 intermediate  
 pressure  $P_2$   
 with  
 $V_i \rightarrow V_2 \rightarrow V_f$

**Path 2:**  
 $w_2 = -P_2 [V_2 - V_i] - P_f [V_f - V_2]$

$\Delta w_2 = \Delta w_1 + \Delta w$



**Clearly,  $\Delta w_2 > \Delta w_1$**

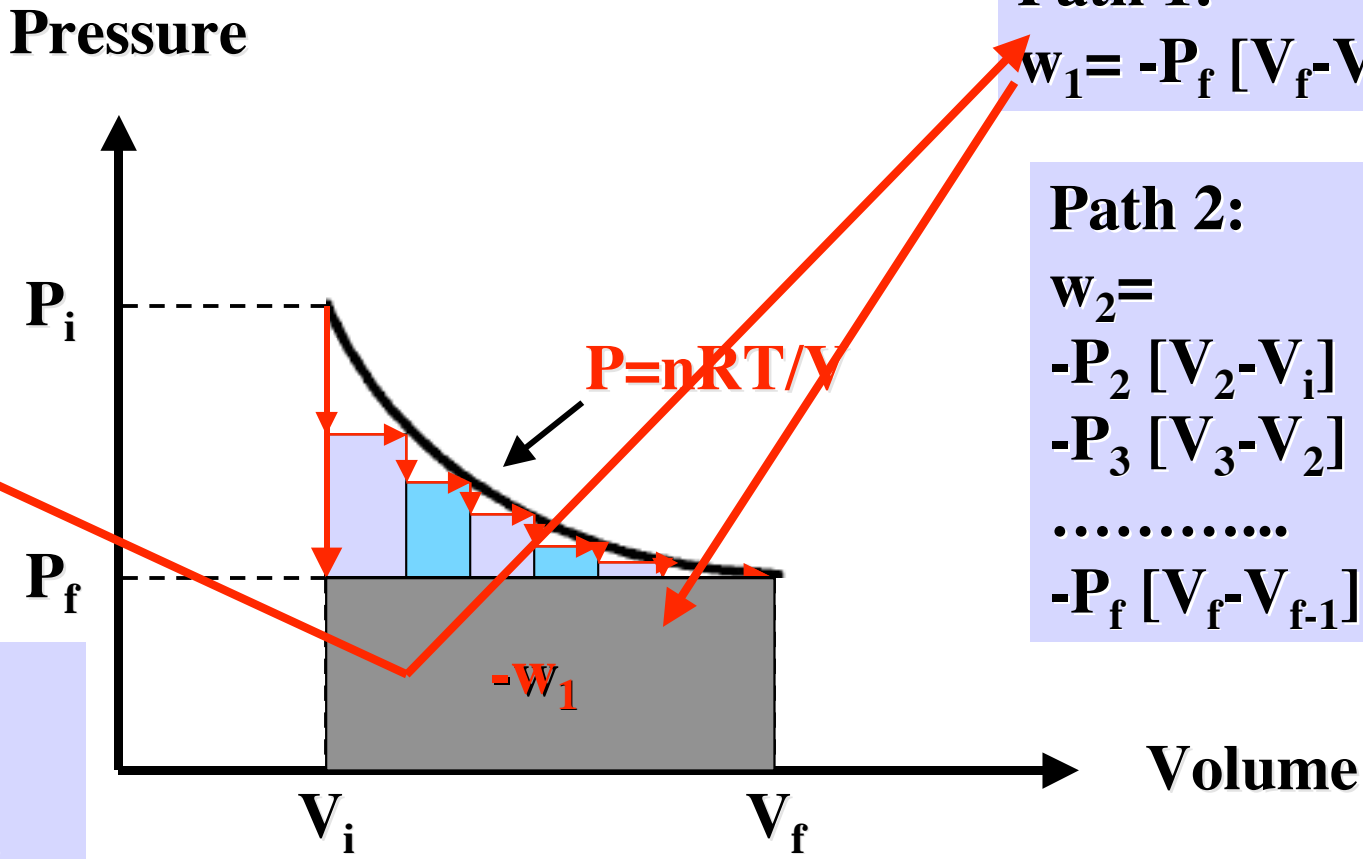
# Work in an Isothermal Expansion: Approaching Reversibility

**Path 1:**  
 $P_i \rightarrow P_f$   
 at start  
 with  
 $V_i \rightarrow V_f$

**Path 1:**  
 $w_1 = -P_f [V_f - V_i]$

**Path 2:**  
 $w_2 =$   
 $-P_2 [V_2 - V_i]$   
 $-P_3 [V_3 - V_2]$   
 .....  
 $-P_f [V_f - V_{f-1}]$

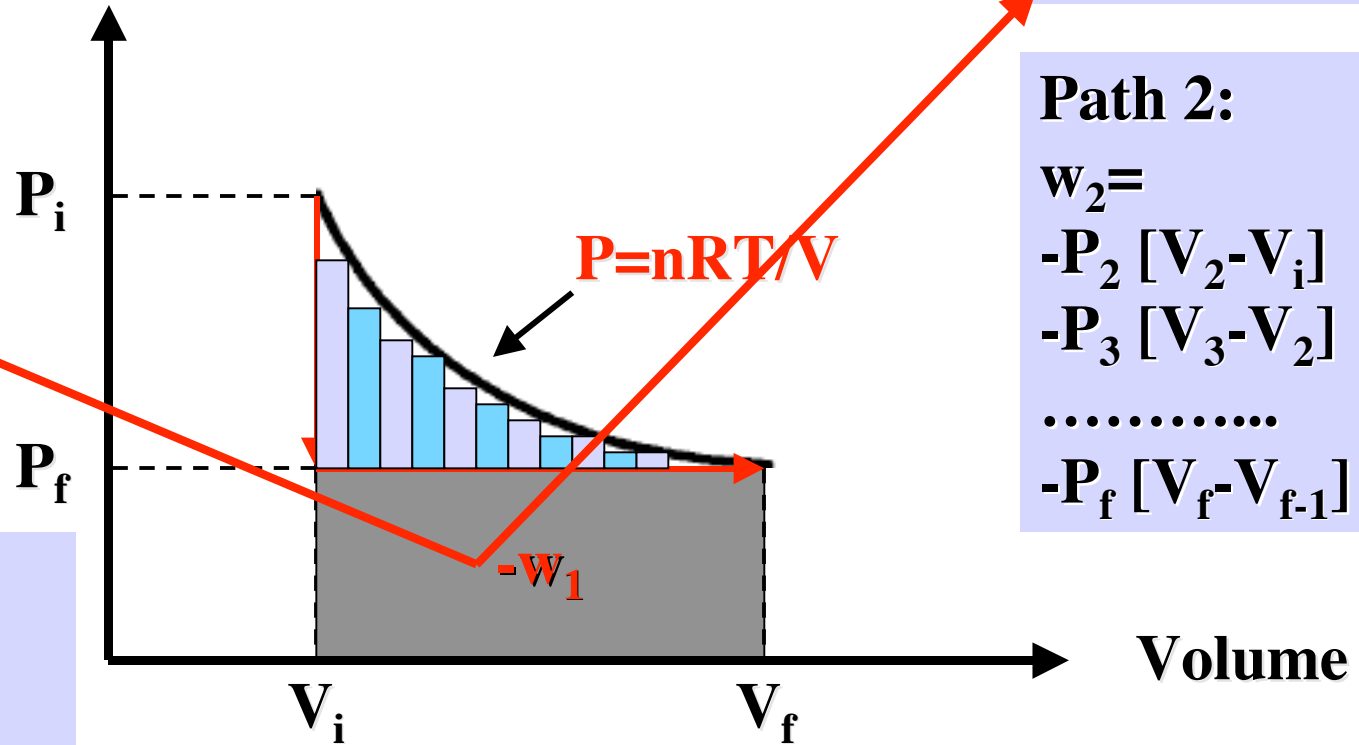
**Path 2:**  
 $P_i \rightarrow P_2 \rightarrow P_3 \rightarrow$   
 $\dots \rightarrow P_f$   
 with  
 $V_i \rightarrow V_2 \rightarrow V_3 \rightarrow$   
 $\dots \rightarrow V_f$



**Clearly,  $|w_2| > |w_1|$**

# Work in an Isothermal Expansion: Approaching Reversibility

Pressure



**Path 1:**  
 $P_i \square P_f$   
 at start  
 with  
 $V_i \square V_f$

**Path 1:**  
 $w_1 = -P_f [V_f - V_i]$

**Path 2:**  
 $w_2 =$   
 $-P_2 [V_2 - V_i]$   
 $-P_3 [V_3 - V_2]$   
 .....  
 $-P_f [V_f - V_{f-1}]$

**Path 2:**  
 $P_i \square P_2 \square P_3 \square$   
 $\square \dots \square P_f$   
 with  
 $V_i \square V_2 \square V_3 \square$   
 $\square \dots \square V_f$

**Clearly,  $w_2 > w_1$**

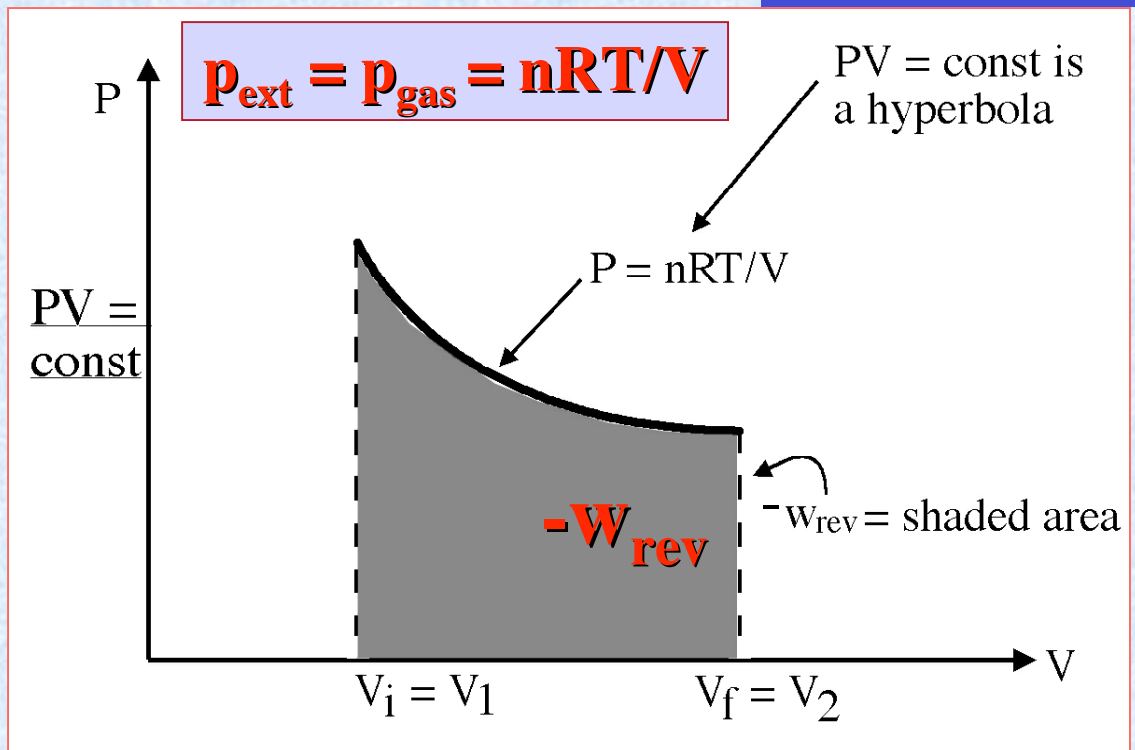
# “True” Reversible, Isothermal Expansion of an Ideal Gas

$$p_{\text{gas}} = p_{\text{ext}}$$

$$p_{\text{gas}} = \frac{nRT}{V}$$

Maximum possible work is done by a gas in a reversible expansion.

$$W_{\text{rev}} = -nRT \ln \frac{V_2}{V_1}$$



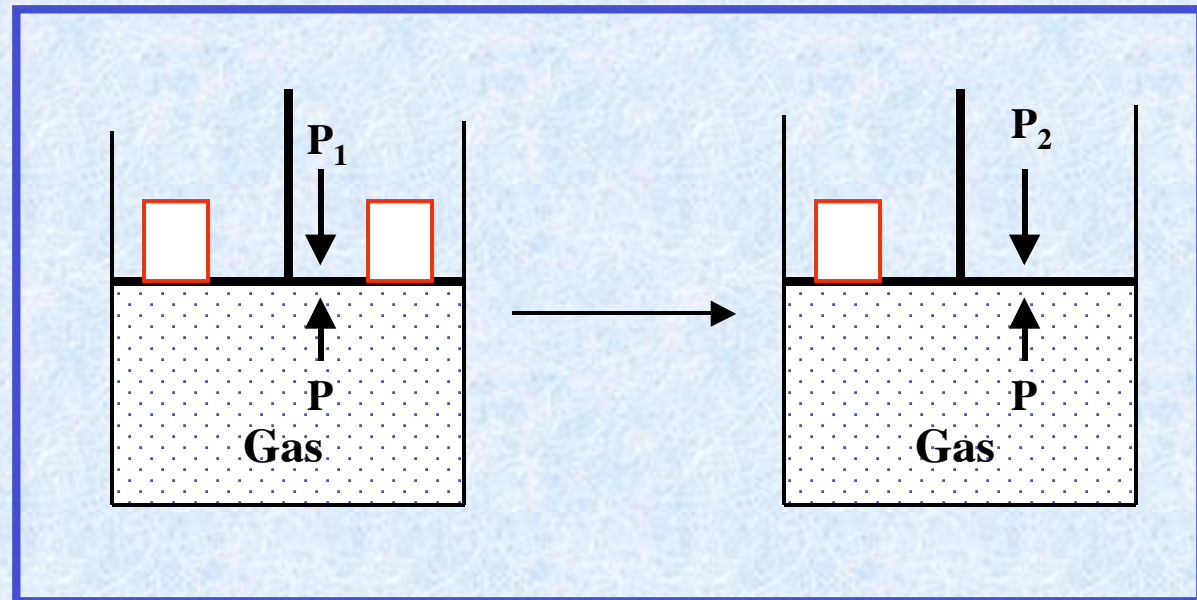
## Quantitative comparison of reversible and irreversible work:

and suddenly drop pressure to:  $P_{\text{ex}} = P_2 = \frac{nRT}{V_2}$

so fast that gas doesn't expand  $\square$

Then expansion  
takes place with  
 $P_{\text{ex}} = P_2$

**Reversible work:**



**Bonus \* Bonus \* Bonus \***  
**Bonus \* Bonus \* Bonus**

## Entropy and the Second Law

**Preliminary statement:** There exists a state function called entropy whose change is given by

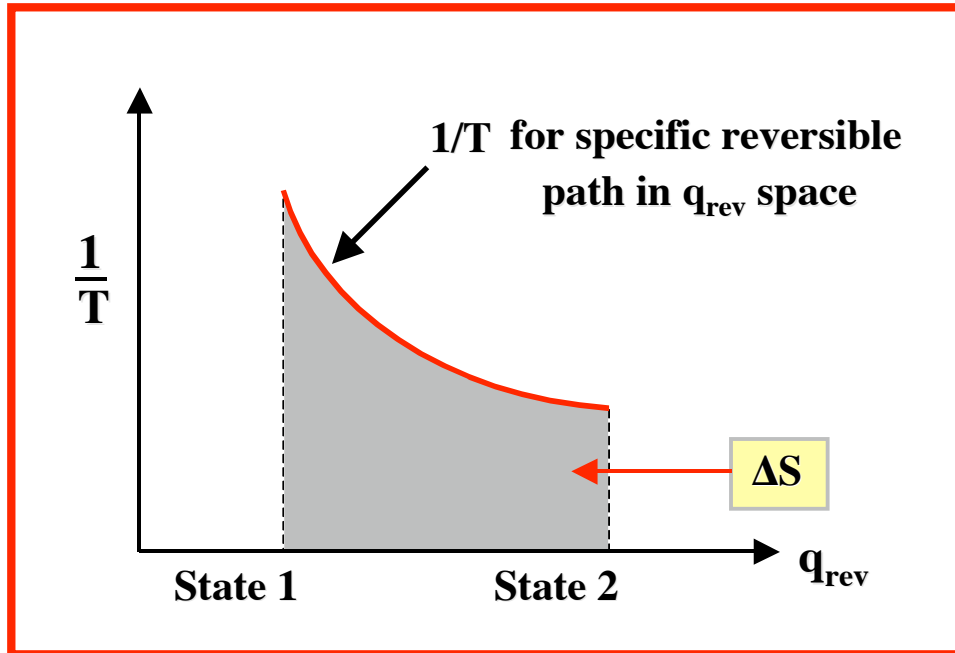
$$\Delta S = \int_1^2 \frac{dq_{\text{rev}}}{T} = \int_1^2 \frac{1}{T} dq_{\text{rev}}$$

Here  $dq_{\text{rev}}$  is an infinitesimal change in the heat added for a reversible process,  $T$  = Kelvin temperature.

**(1) Choose a reversible path**

**(3) Divide  $dq_{\text{rev}}$  by  $T$  at each point**

**If  $q_{\text{rev}}$  were an ordinary well defined variable (state function) like  $P$ ,  $V$  could think of it this way:**



**(graph is misleading because  $q$  is not an ordinary variable!)**

**Thus, over any path between the same initial and final states (reversible or irreversible)  $\Delta S$  has the same value.**



## **The Second Law**

**The simplest way to state the second law is for an isolated system.  
This is a system for which  $dq = 0$ , and  $dw = 0$ .**

**$\Delta S = 0$  for a reversible change**

**$\Delta S > 0$  for an irreversible change**

**(corollary :  $\Delta S < 0$  is impossible for an **isolated** system).**

**The word spontaneous is used interchangeably with irreversible to describe processes that are observed in nature to "proceed on their own".**

**Since we can always combine the system together with surroundings to form an isolated system which is the universe, we can restate the 2nd Law:**

**$\Delta S$  (universe) < 0 impossible (never observed)**

## Entropy Calculations

**1) Cardinal Rule: Can only calculate entropy change if choose a reversible path.**

**3)  $\Delta S$  for isothermal process (reversible)  $T = \text{const}$**

$\int_1^2 dq_{\text{rev}}$  = sum of heat changes over path. Total is  $q_{\text{rev}}$  or heat added going from state 1 to 2 over reversible path.

For an ideal monatomic gas  $E = (3/2) RT$

$$\Delta E = q + w = 0 \quad \square \quad w = -q$$

For an ideal gas,  $P = \frac{nRT}{V}$  } In a reversible process,  $P=P_{\text{ext}}$  and  $V$  is not constant.

$$\Delta S = nR \ln (V_2 / V_1) \text{ Ideal gas isothermal change.}$$

Note this last case is **NOT** inconsistent with the 2nd law!

**System** entropy can decrease as long as entropy of **universe** either increases or stays the same. If system entropy decreases, entropy of surroundings must increase.

As we shall see later, the fact that we need to include both the system and surroundings when considering the Second Law makes the  $\Delta S$  function “**inconvenient**”.

## Temperature Dependence of Entropy

$$\Delta S = \int_1^2 \frac{dq_{\text{rev}}}{T}$$

For constant pressure process

For infinitesimal change  $dq_{\text{rev}} = nC_p dT$   
[Now assume  $C_p$  independent of  $T$ ]

$$\Delta S_p = nC_p \ln (T_2 / T_1)$$

Assumes  $C_p$ ,  $C_v$  are constant  
over range  $T_1 \leq T_2$

For an ideal gas

$$C_p = (3/2)R + R = (5/2)R$$

Note that  $\Delta S_p$ ,  $\Delta S_v$  are **not** the same. Cannot be between same initial and final states! ( $T_1$ ,  $T_2$  can be same but  $P_1$ ,  $P_2$  and  $V_1$ ,  $V_2$  must be different).

### Absolute Entropies and the Third Law

In same way can set up an arbitrary scale for  $\Delta S_f^\circ$ . As it turns out, can **also** set up an **absolute scale** for entropy.

## Third Law of Thermodynamics

But  $\Delta S = \int [dq_{\text{rev}}/T]$

$$dq_{\text{rev}} = C_p dT$$

$$\Delta S = S_{T_F} - S_0 = S_{T_F} - 0 = S_{T_F}$$

**Note: Really cannot take  $C_p$  independent of  $T$  here because are going from absolute zero to some finite  $T$ . Most substances go from solid to liquid to gas over this range!**

$S_{298}^\circ \equiv$  Standard absolute entropy:  $T_F = 298 \text{ K}$  and  $P = 1 \text{ atm}$ .