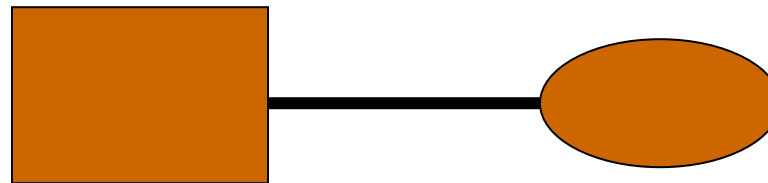
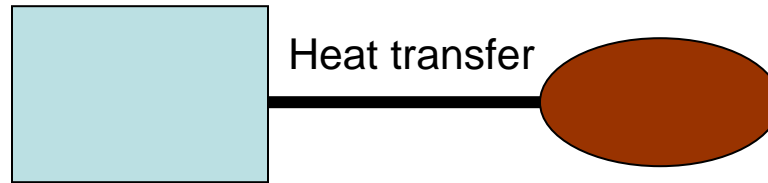




# Chapter 19

## Chemical Thermodynamics

# Zeroth Law of Thermodynamics



Thermal Equilibrium

Same Temperature

Equilibrium – unchanged with time

# First Law of Thermodynamics

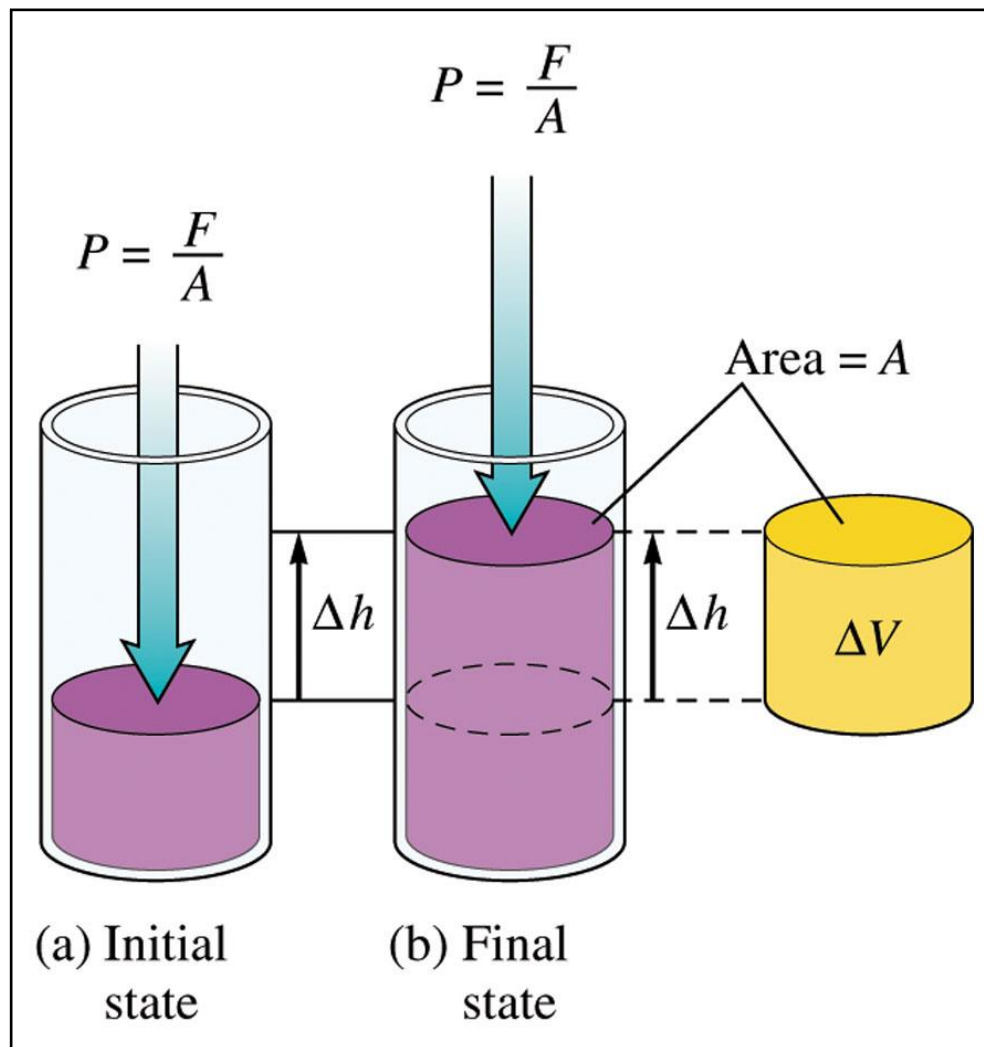
$$E(\text{system}) + E(\text{surrounding}) = \text{constant}$$

$$\Delta E = q + w$$

**TABLE 5.1 • Sign Conventions for  $q$ ,  $w$ , and  $\Delta E$**

For $q$	+ means system <i>gains</i> heat	– means system <i>loses</i> heat
For $w$	+ means work done <i>on</i> system	– means work done <i>by</i> system
For $\Delta E$	+ means <i>net gain</i> of energy by system	– means <i>net loss</i> of energy by system

$$w = -P_{\text{ext}} \Delta V$$



# Driving Force of a Process

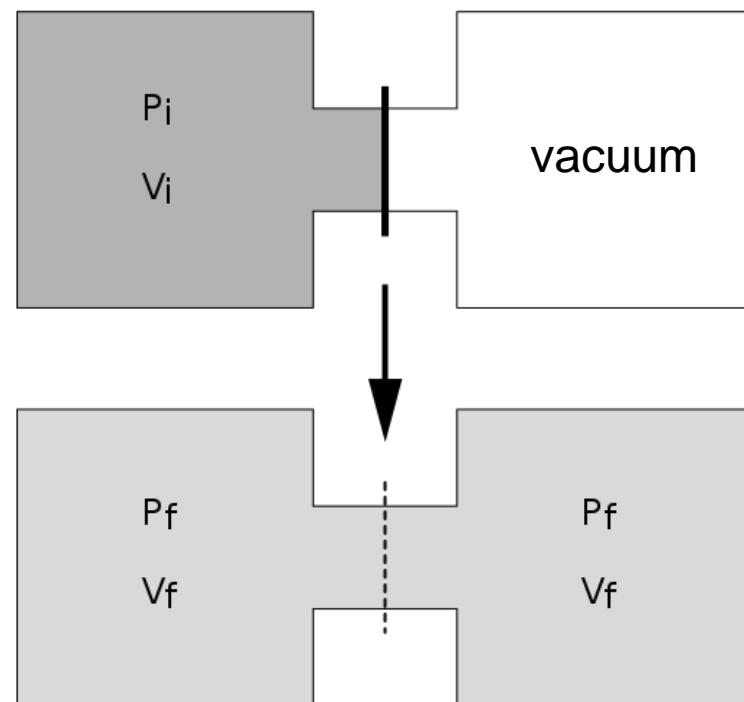
Case study 1: Free expansion

$$q = 0$$

$$w = -P_{\text{ext}}\Delta V = 0$$

$$\Delta E = q + w = 0$$

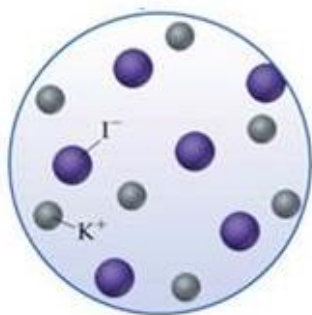
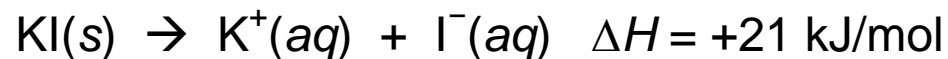
Thermally isolated



This is a spontaneous process and  $\Delta E = 0$ .

# Driving Force of a Process

## Case study 2: Dissolution



Weak hydration energy

## Case study 3: Melting

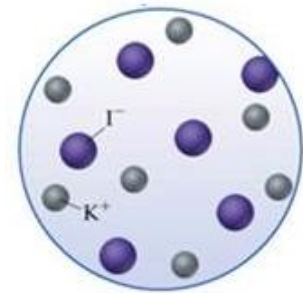
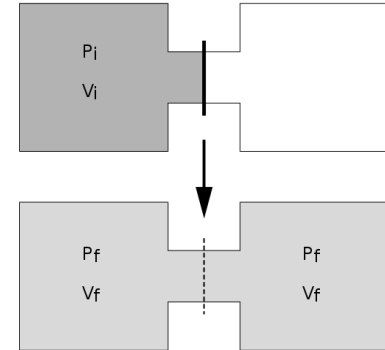


These are spontaneous processes but  $\Delta E > 0$ !

# Driving Force of a Process

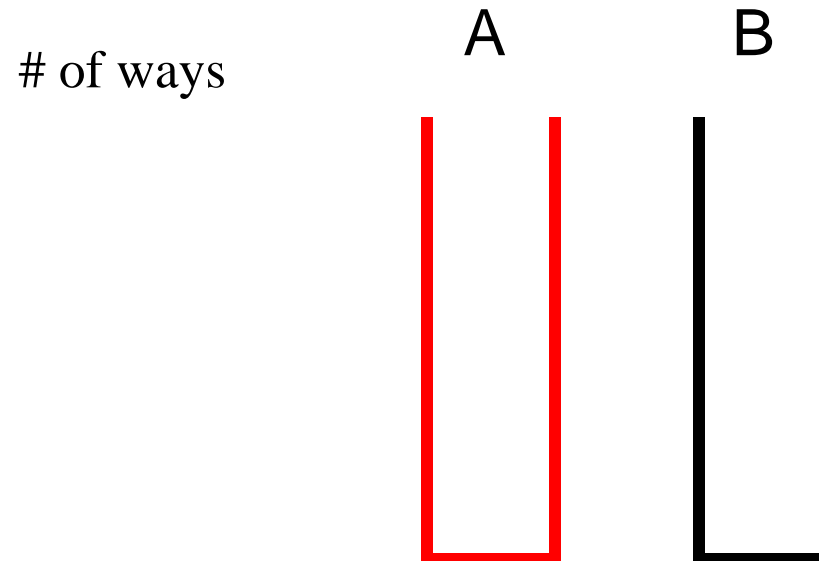
What's in common?

Increase in randomness or disorder



# Likelihood

Balls in a container



Both in A

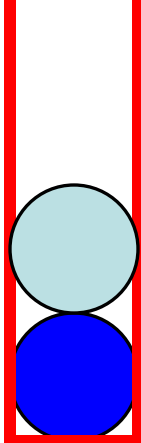
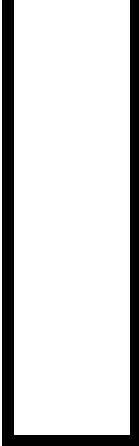
Both in B

Each has one



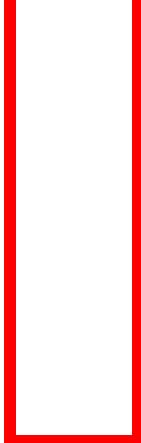
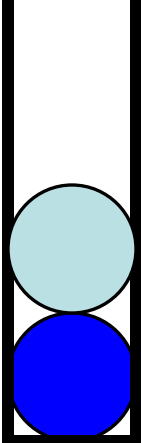
# Likelihood

Balls in a container

	# of ways	A	B
Both in A	1		
Both in B			
Each has one			

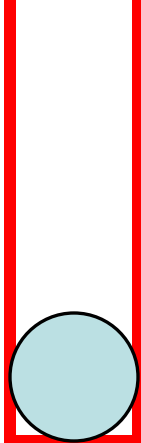
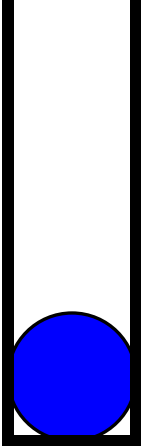
# Likelihood

Balls in a container

	# of ways	A	B
Both in A	1		
Both in B	1		
Each has one			

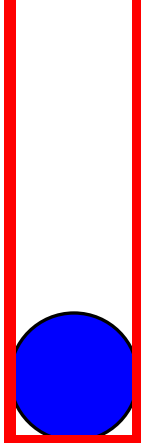
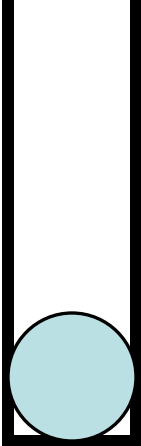
# Likelihood

Balls in a container

	# of ways	A	B
Both in A	1		
Both in B	1		
Each has one	1		

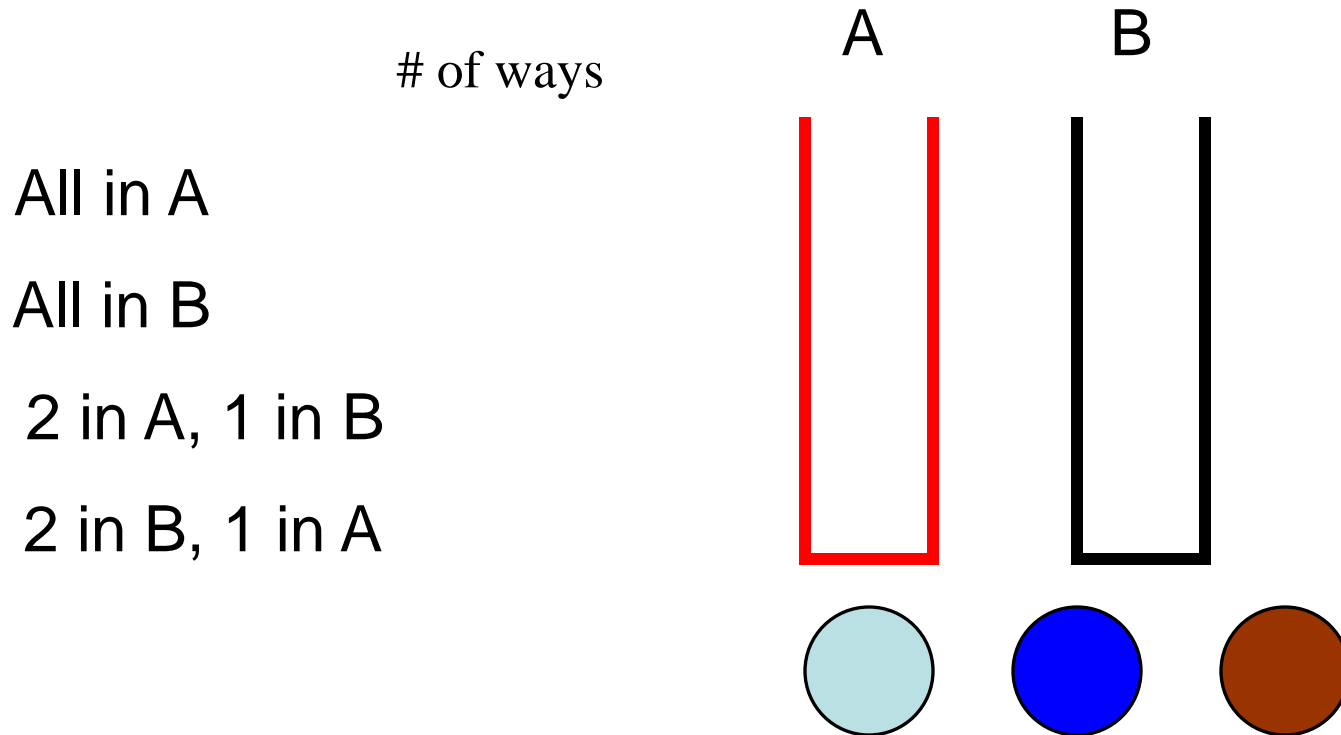
# Likelihood

Balls in a container

	# of ways	A	B
Both in A	1		
Both in B	1		
Each has one	2		

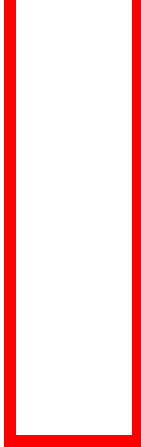
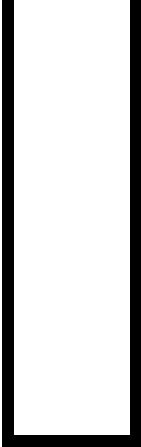
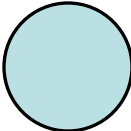
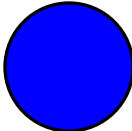
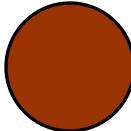
# Likelihood

Balls in a container



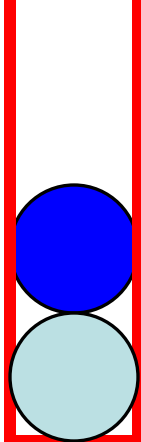
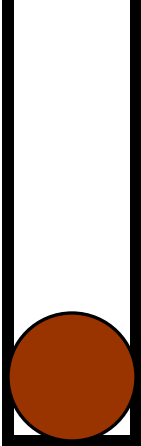
# Likelihood

Balls in a container

	# of ways	A	B
All in A	1		
All in B	1		
2 in A, 1 in B			
2 in B, 1 in A			
			
			

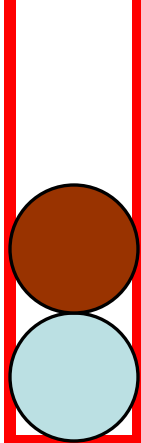
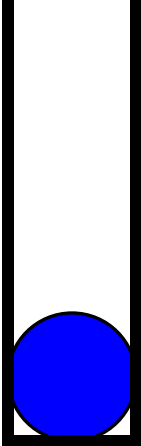
# Likelihood

Balls in a container

	# of ways	A	B
All in A	1		
All in B	1		
2 in A, 1 in B	1		
2 in B, 1 in A	1		

# Likelihood

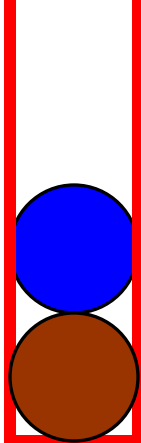
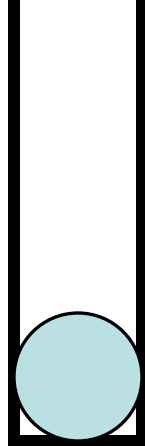
Balls in a container

	# of ways	A	B
All in A	1		
All in B	1		
2 in A, 1 in B	2		
2 in B, 1 in A			



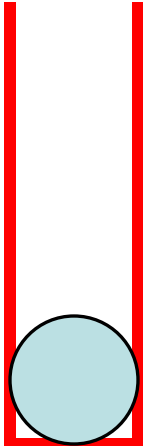
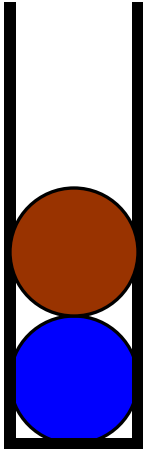
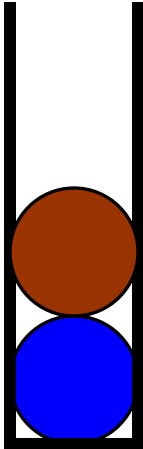
# Likelihood

Balls in a container

	# of ways	A	B
All in A	1		
All in B	1		
2 in A, 1 in B	3		
2 in B, 1 in A			

# Likelihood

Balls in a container

	# of ways	A	B
All in A	1		
All in B	1		
2 in A, 1 in B	3		
2 in B, 1 in A	3		

# Likelihood

Balls in a container

What about 20 balls in two containers

$$\# \text{ of ways} = \frac{N!}{n_a! n_b!}$$

$N$ : Total # of balls

$n_a$ : # of balls in A

$n_b$ : # of balls in B

$$N! = N \times (N - 1) \times (N - 2) \times \dots \times 1$$

# Likeliness

Randomly place 20 balls in two containers

	Balls in A	Balls in B	# of ways	
State A	20	0	1	Not likely
State B	19	1	20	
State C	10	10	184756	Very likely

# Likeliness

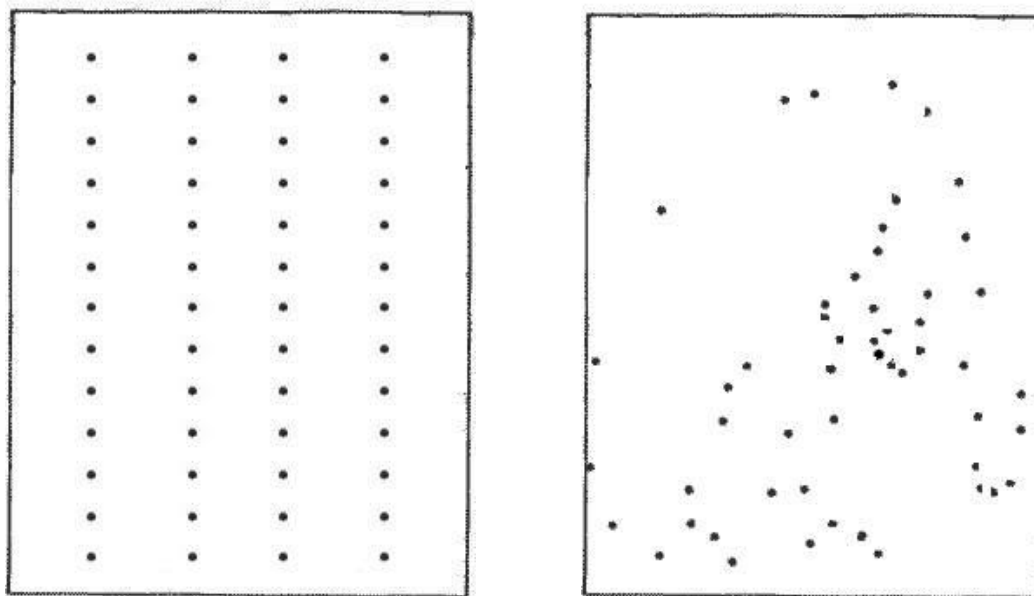
Randomly place one mole of molecules in two containers

	Balls in A	Balls in B	# of ways	
State D	1 mole	0	1	Impossible
State E	0.5 mole	0.5 mole	Many many	Observed

*States of greater disorder are favored over more ordered states!*

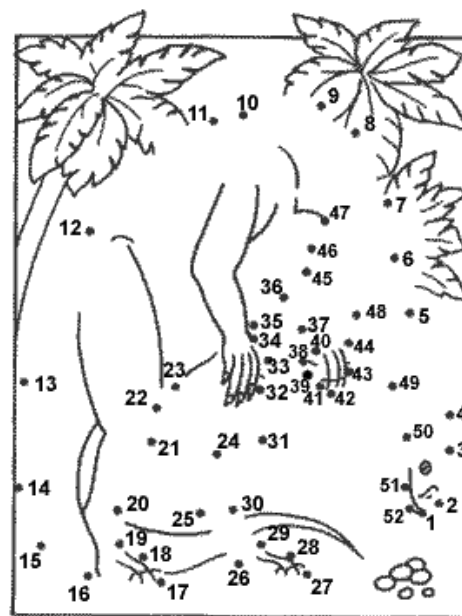
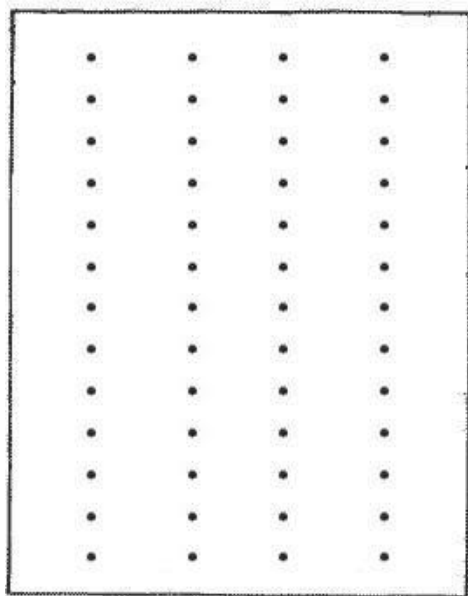
*States of greater disorder are favored over more ordered states!*

Order or Disorder ?



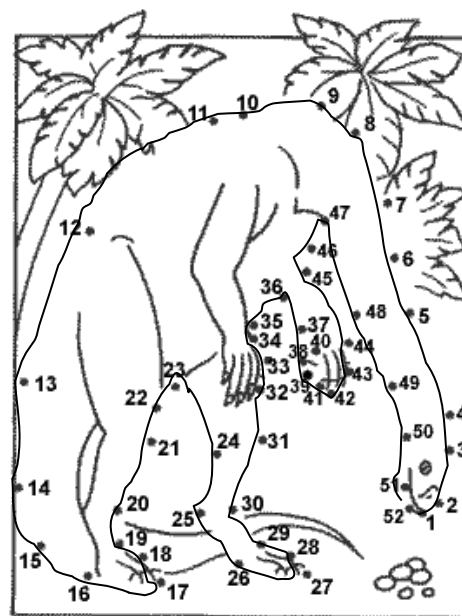
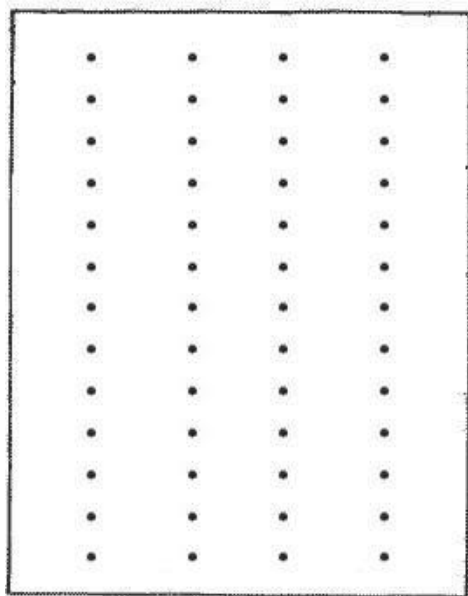
*States of greater disorder are favored over more ordered states!*

Order or Disorder ?



*States of greater disorder are favored over more ordered states!*

Order or Disorder ?





*States of greater disorder are favored over more ordered states!*

Outside

	Balls in A	Balls in B	# of ways (inside)	
State D	1 mole	0	1	
State E	0.5 mole	0.5 mole	Many many	Greater disorder

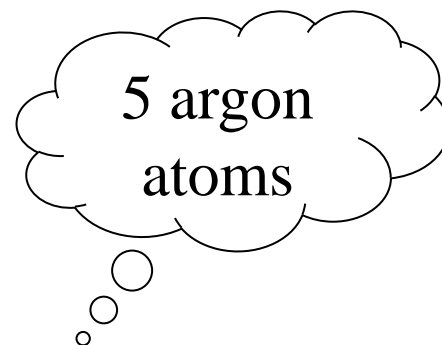
We measure “disorder” by the number of ways that the **inside** can be arranged, so that from the **outside** it looks the same!



## Learning Check

Which one of the following has the largest disorder?

1. Five atoms of Argon
2. One molecule of  $\text{CH}_4$
3. Two molecules of oxygen



## Learning Check

Which one of the following has the largest disorder?

1. One mole of Argon
2. One mole of water
3. One mole of methane



*States of greater disorder are favored over more ordered states!*

## *Change in Energy Form?*

$q$  (heat): Disordered form of energy

$w$  (work): Ordered form of energy

# Isothermal **Expansion** of an Ideal Gas

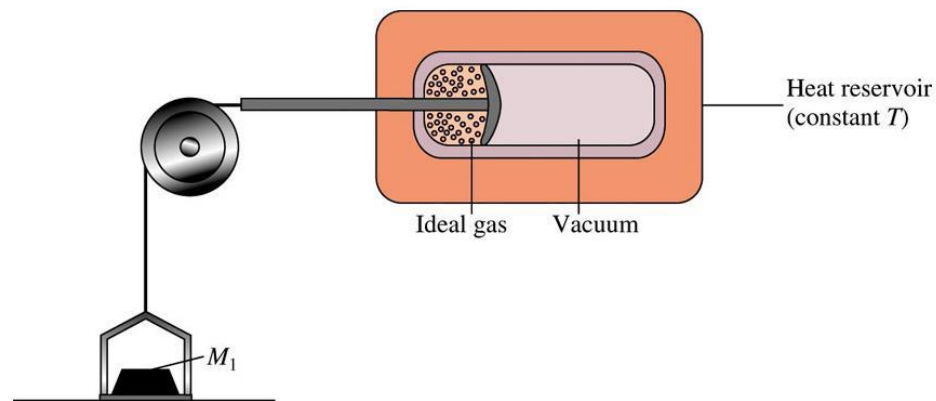
$$PV = nRT$$

## Isothermal Process

$$P_1V_1 = P_2V_2$$

$M_1 \rightarrow 0$  Free expansion

$\Rightarrow w = 0$



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# Isothermal **Expansion** of an Ideal Gas

$$M_1 \rightarrow M_1/4$$

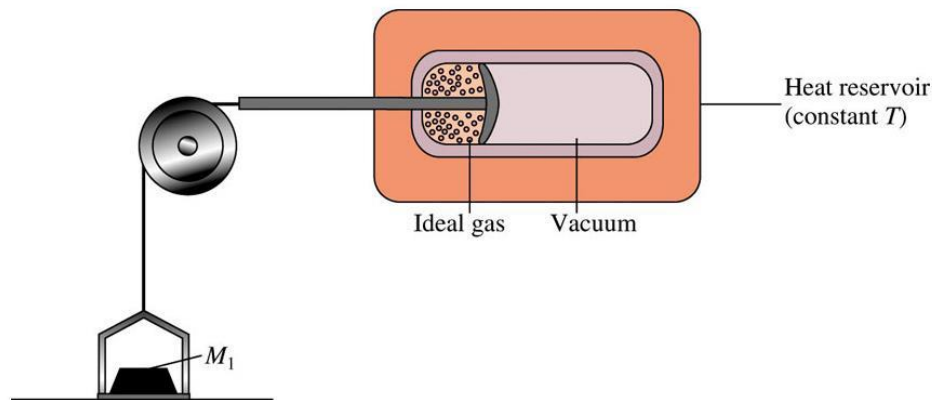
$$P_2 = \frac{P_1}{4} \quad \Rightarrow \quad V_2 = 4V_1 \quad \Rightarrow \quad w = -\frac{P_1}{4}(4V_1 - V_1) = -\frac{3}{4}P_1V_1$$

$$w = -\frac{3}{4}P_1V_1$$

Do we have the same amount of work done for

$$M_1 \rightarrow M_1/2 \rightarrow M_1/4 ?$$

(i)                      (ii)



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# Isothermal **Expansion** of an Ideal Gas

(i)  $M_1 \rightarrow M_1/2$

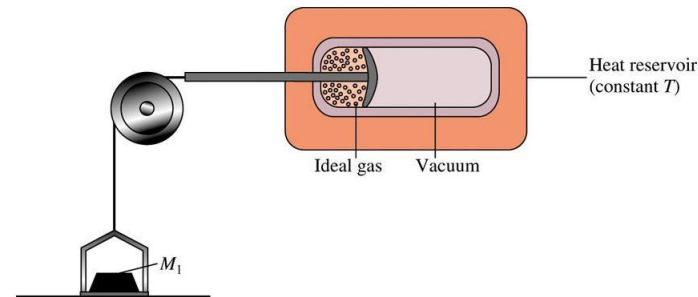
$$P_2 = \frac{P_1}{2} \Rightarrow V_2 = 2V_1 \Rightarrow w = -\left(\frac{P_1}{2}\right)(2V_1 - V_1) = -\frac{1}{2}P_1V_1$$

(ii)  $M_1/2 \rightarrow M_1/4$

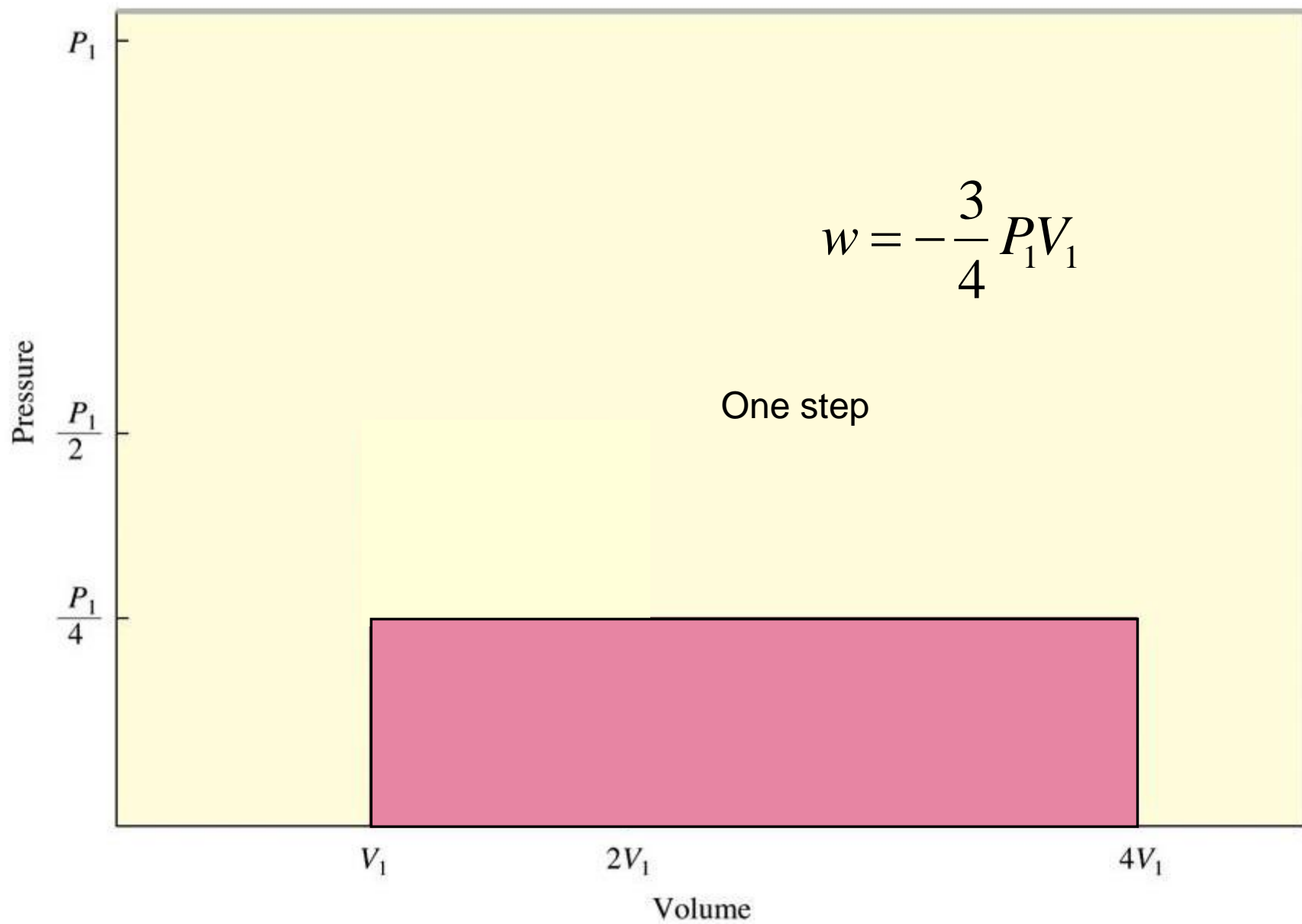
$$P_3 = \frac{P_2}{2} \Rightarrow V_3 = 2V_2 \Rightarrow w = -\left[\frac{1}{2}\left(\frac{P_1}{2}\right)\right][2(2V_1) - 2V_1] = -\frac{1}{2}P_1V_1$$

Total work done in two steps =  $-P_1V_1$

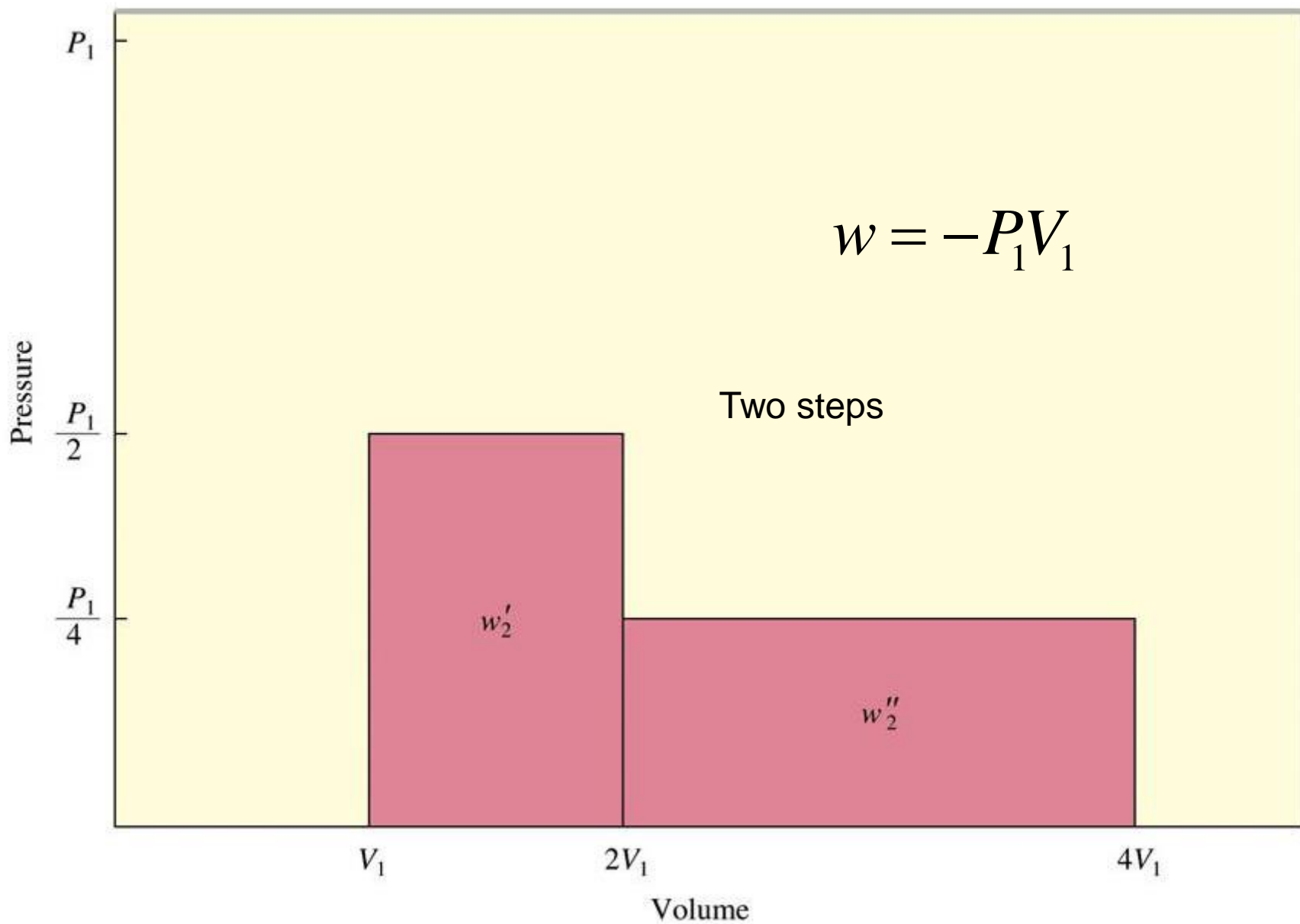
Total work done in one step =  $-\frac{3}{4}P_1V_1$

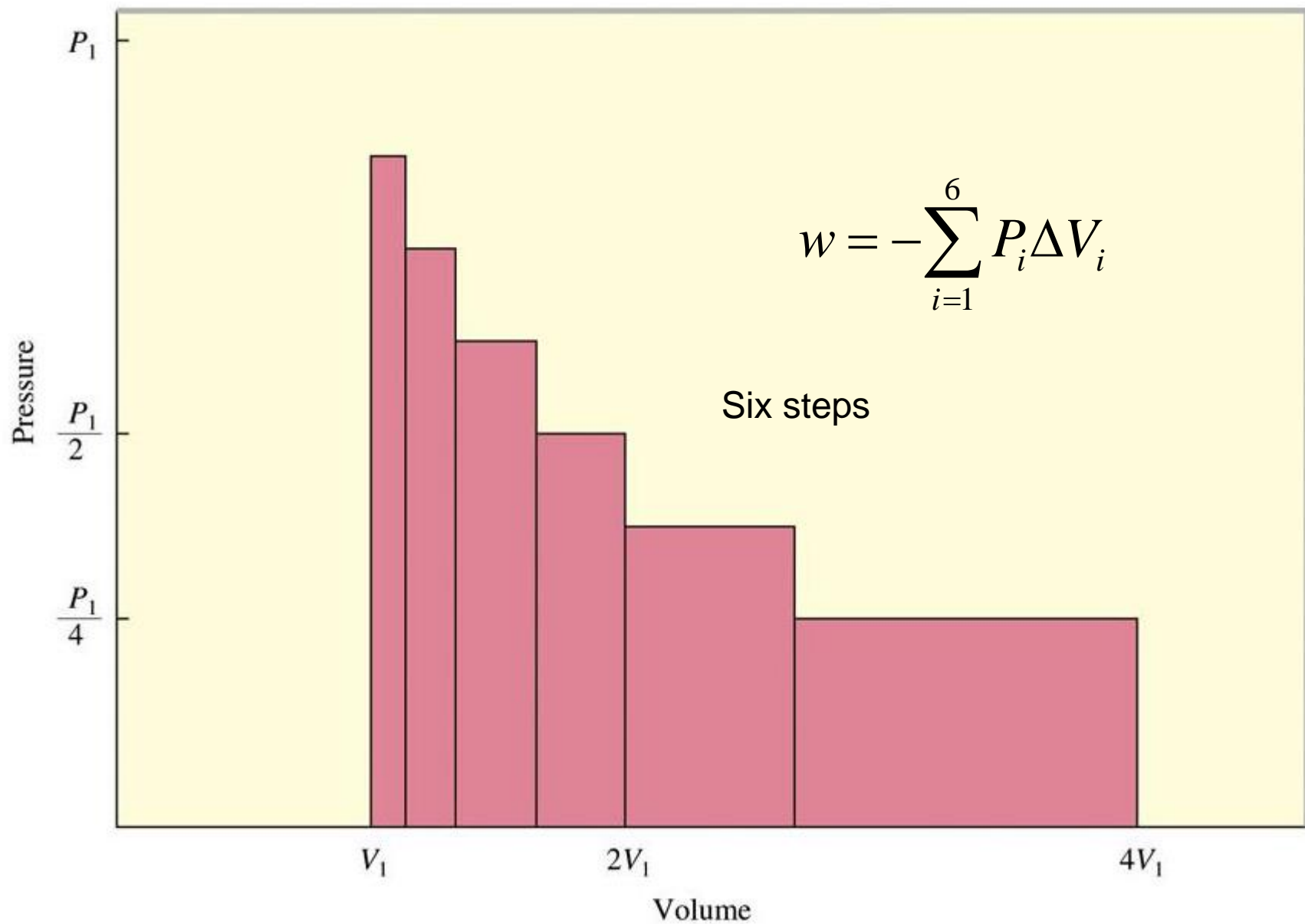


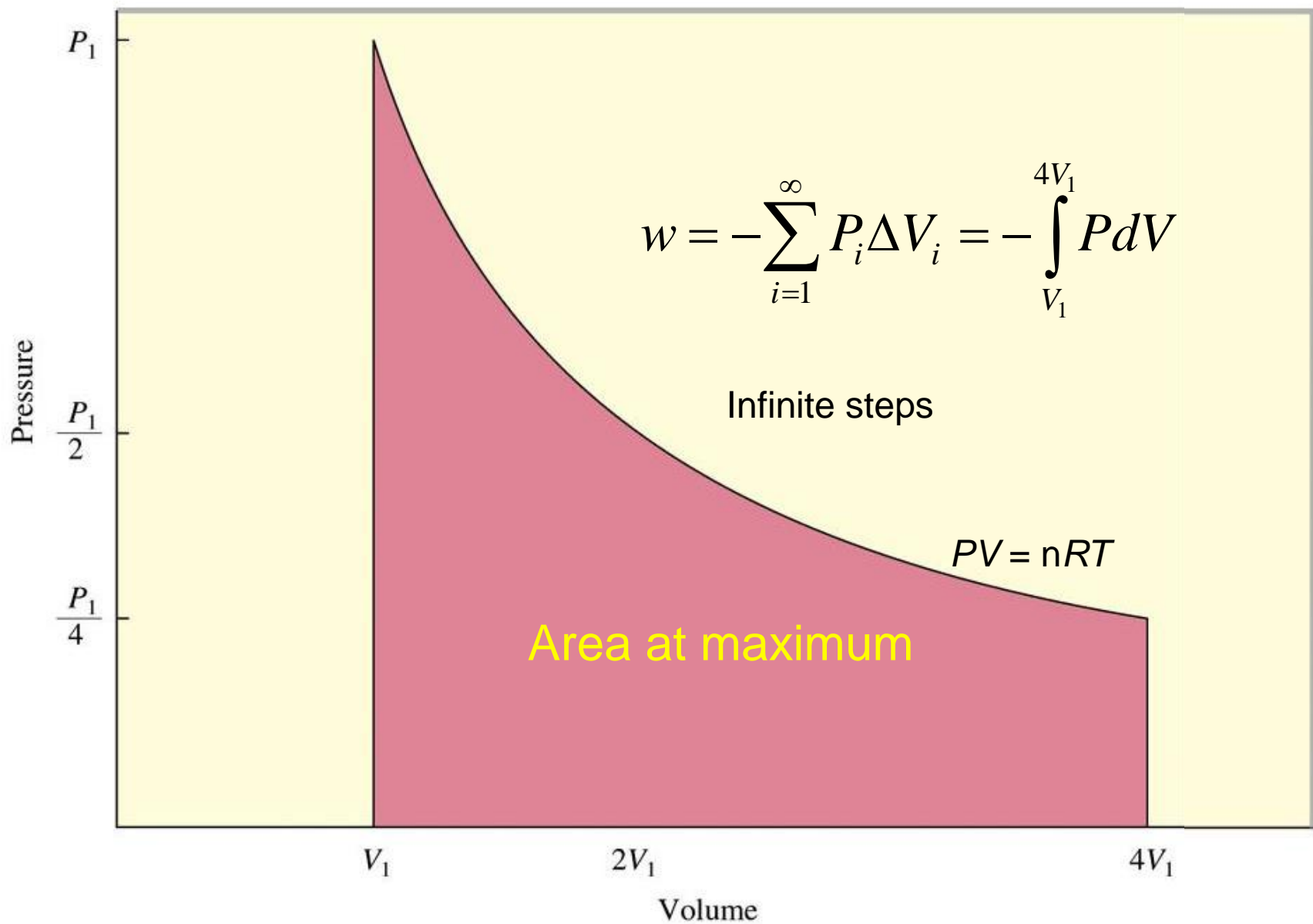
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# Reversible Processes

In thermodynamics, a **reversible** process is a process that occurs when the system is **infinitesimally close to equilibrium at each step** throughout the entire process.

**Hypothetical** examples:

Expansion in infinite steps ( $P_{\text{system}} = P_{\text{ext}}$ )

**Real-life** examples:

Water boiling; ice melting

Coexistence  $\rightarrow$  Equilibrium

**TABLE 10.3** Summary of the Isothermal Expansion

	Number of Steps	$w$
Expansion (constant $T$ )	0 (no mass)	0
	1	$-0.75P_1V_1$
	2	$-1P_1V_1$
	4	$-1.16P_1V_1$
	$\infty$	$-1.4P_1V_1$

Work done by the system is at maximum for reversible processes.

$\Delta E = 0$  at constant  $T$  for ideal gas (has kinetic energy only), i.e.  $0 = w + q$

# Heat Change of a Reversible Isothermal Expansion

$$w = -\sum_{i=1}^{\infty} P_i \Delta V_i$$

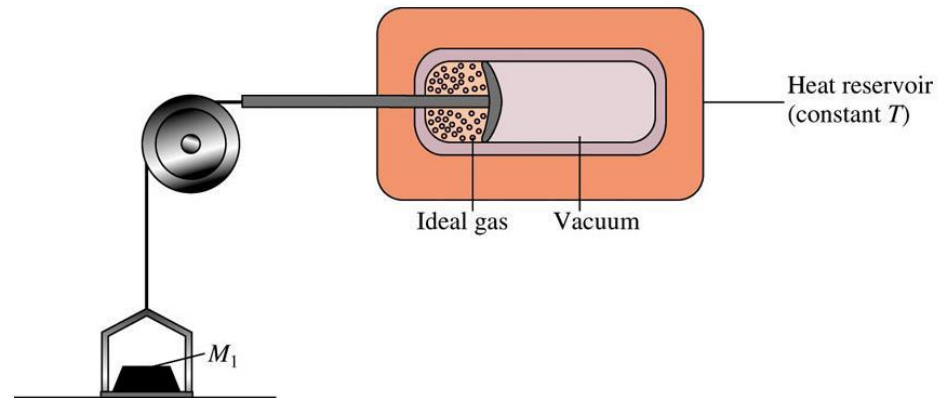
$$w = -\int_{V_0}^{V_f} P_{ext} dV$$

$$P_{ext} = P = \frac{nRT}{V} \quad \text{For ideal gas only}$$

$$w_{rev} = -nRT \ln \left( \frac{V_f}{V_0} \right)$$

State functions

$$q_{rev} = nRT \ln \left( \frac{V_f}{V_0} \right)$$



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# Isothermal Compression of an Ideal Gas

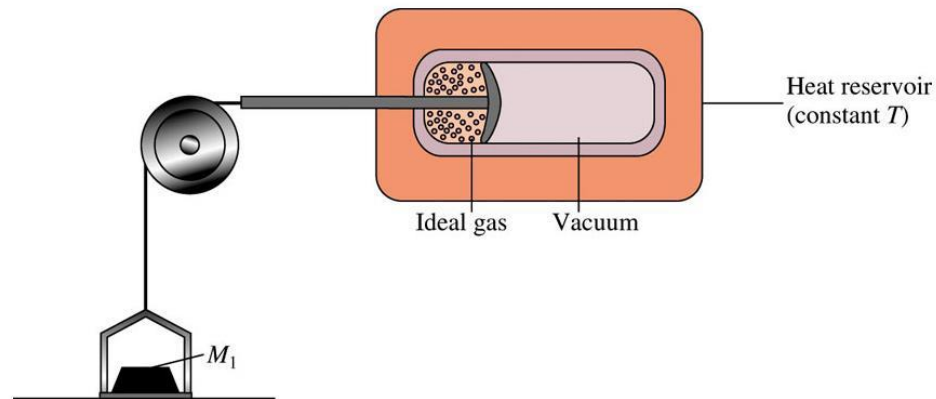
$$M_1/4 \rightarrow M_1$$

$$P_1/4 \rightarrow P_1 \Rightarrow 4V_1 \rightarrow V_1$$

$$w = -P_1(V_1 - 4V_1) = 3P_1V_1$$

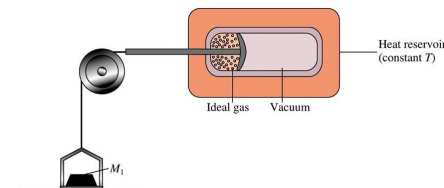
$$M_1/4 \rightarrow M_1/2 \rightarrow M_1$$

$$\begin{aligned} w &= -\frac{P_1}{2}(2V_1 - 4V_1) - P_1(V_1 - 2V_1) \\ &= 2P_1V_1 \end{aligned}$$



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**TABLE 10.3** Summary of the Isothermal Expansion and Compression Experiments



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	Number of Steps	$w$	$q$
Expansion (constant $T$ )	0 (no mass)	0	0
	1	$-0.75P_1V_1$	$0.75P_1V_1$
	2	$-1P_1V_1$	$1P_1V_1$
	4	$-1.16P_1V_1$	$1.16P_1V_1$
	$\infty$	$-1.4P_1V_1$	$1.4P_1V_1$
Compression (constant $T$ )	1	$3P_1V_1$	$-3P_1V_1$
	2	$2P_1V_1$	$-2P_1V_1$
	4	$1.67P_1V_1$	$-1.67P_1V_1$
	$\infty$	$1.4P_1V_1$	$-1.4P_1V_1$

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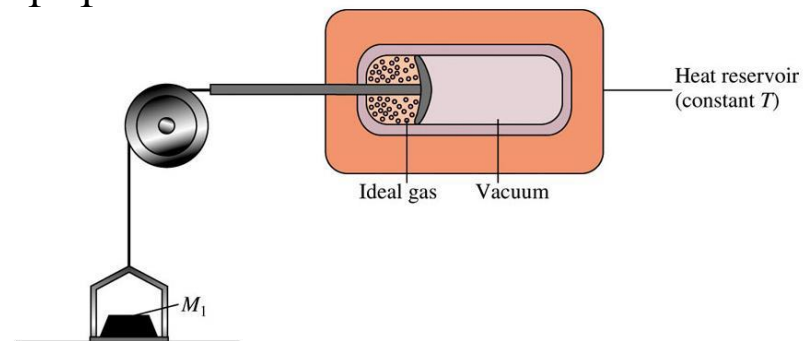
# Isothermal Cyclic **Expansion**-**Compression** of an Ideal Gas

One-step expansion and compression (**system unchanged**):

$$w_{\text{net}} = -0.75P_1V_1 + 3P_1V_1 = 2.25P_1V_1$$

$$\Delta E = w_{\text{net}} + q_{\text{net}} = 0$$

$$\therefore q_{\text{net}} = -2.25P_1V_1$$



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*Ordered energy transfer (work) transformed to  
disordered energy transfer (heat)*

*– Something in the surrounding has changed!*

# Isothermal Cyclic **Expansion**-**Compression** of an Ideal Gas

One step:  $w_{\text{net}} = -q_{\text{net}} = 2.25 P_1 V_1$

Two steps:  $w_{\text{net}} = -q_{\text{net}} = P_1 V_1$

Four steps:  $w_{\text{net}} = -q_{\text{net}} = 0.51 P_1 V_1$

	Number of Steps	$w$
Expansion (constant $T$ )	0 (no mass)	0
	1	$-0.75P_1V_1$
	2	$-1P_1V_1$
	4	$-1.16P_1V_1$
	$\infty$	$-1.4P_1V_1$
Compression (constant $T$ )	1	$3P_1V_1$
	2	$2P_1V_1$
	4	$1.67P_1V_1$
	$\infty$	$1.4P_1V_1$

Path dependent, not a state function

**The system is unchanged.**

**The surrounding has changed!**

# Isothermal Cyclic **Expansion**-**Compression** of an Ideal Gas

**Reversible** expansion and compression (system unchanged):

$$w_{\text{rev, net}} = -1.4P_1V_1 + 1.4P_1V_1 = 0$$

$$\therefore q_{\text{rev, net}} = +1.4P_1V_1 - 1.4P_1V_1 = 0$$

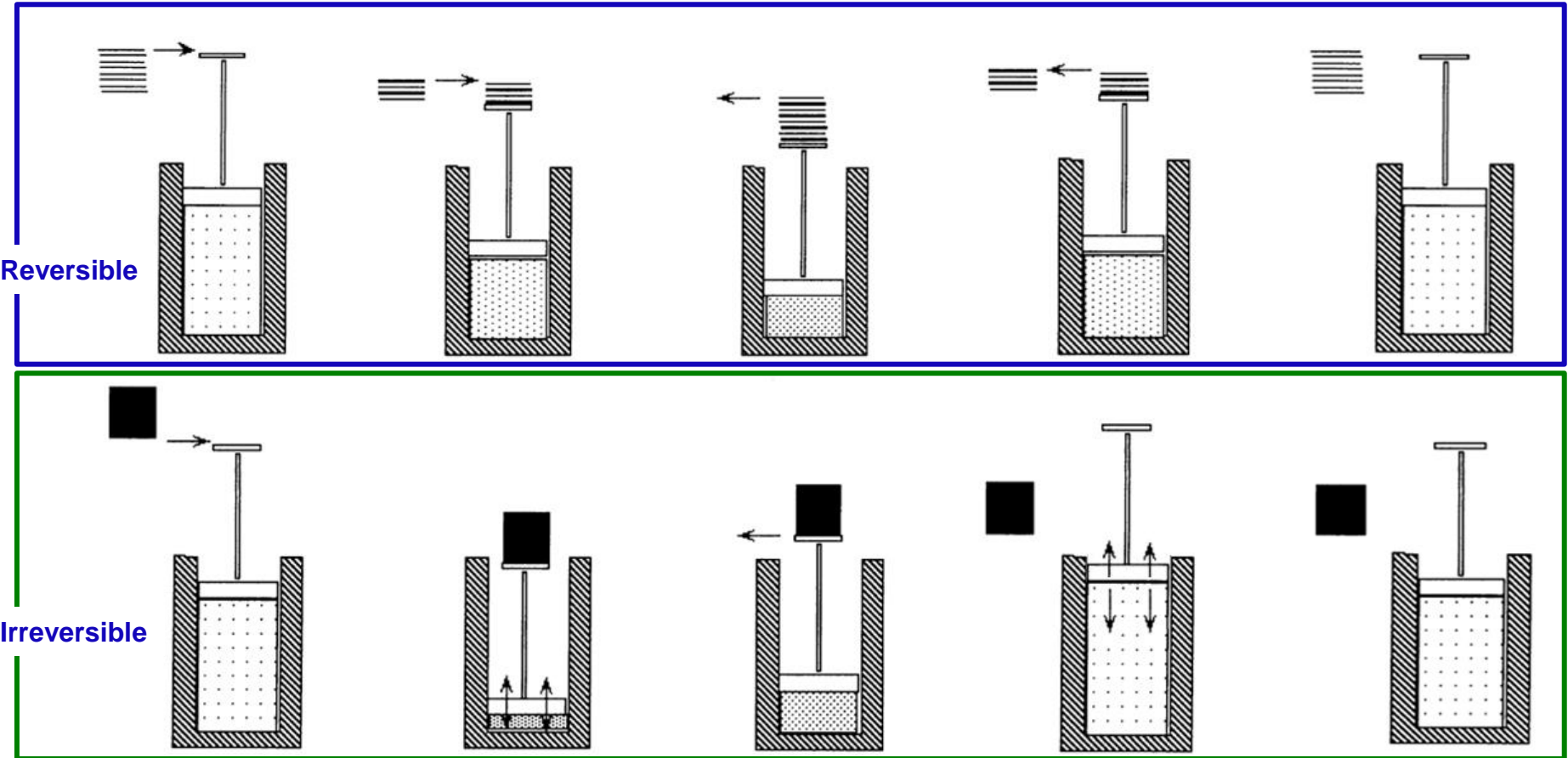
No net change after a cyclic path

➡  $q_{\text{rev}}$  and  $w_{\text{rev}}$  are **state functions**! – path is defined

	Number of Steps	$w$
Expansion (constant $T$ )	0 (no mass)	0
	1	$-0.75P_1V_1$
	2	$-1P_1V_1$
	4	$-1.16P_1V_1$
	$\infty$	$-1.4P_1V_1$
Compression (constant $T$ )	1	$3P_1V_1$
	2	$2P_1V_1$
	4	$1.67P_1V_1$
	$\infty$	$1.4P_1V_1$

**Both the system and the surrounding are unchanged.**

# Isothermal Cyclic Compression and Expansion



# Isothermal Cyclic Expansion-Compression of an Ideal Gas

Reversible process:  $w_{\text{rev, net}} = q_{\text{rev, net}} = 0$

System and surrounding are returned to their original conditions.

Irreversible process:  $w_{\text{net}} > 0$        $q_{\text{net}} < 0$   
(Finite steps)

System is returned to the original condition but **NOT** the surrounding.

All real compression or expansion processes are

**thermodynamically irreversible!**

(Energy distribution changed to a more disordered form)

# Second Law of Thermodynamics

*States of greater disorder are favored over more ordered states!*

*Energy **spontaneously** tends to flow only from being concentrated in one place to becoming diffused or dispersed and spread out.*

# Entropy: Definition of Disorder in Thermodynamics

## Microscopic

Number of microstates  
 $\Omega$

Balls in A	Balls in B	# of ways
1 mole	0	1
0.5 mole	0.5 mole	Many many

## Macroscopic

Entropy  
 $S$

$S$  is an extensive state function like  $E$  and  $H$

For a combined system A+B

$$\Omega_{A+B} = \Omega_A \times \Omega_B$$

$$S_{A+B} = S_A + S_B$$

$$S \propto \ln \Omega$$



$$S = k_B \ln \Omega$$

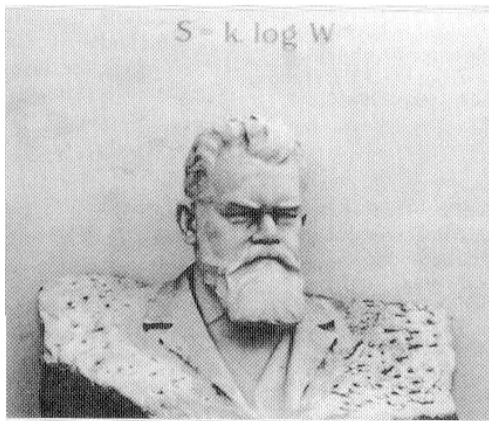
# Entropy: Definition of Disorder in Thermodynamics

$$S = k_B \ln \Omega$$

State function

$\Omega$  = Number of ways corresponding to a given state

$k_B$  = Boltzmann's constant =  $R/N_A$





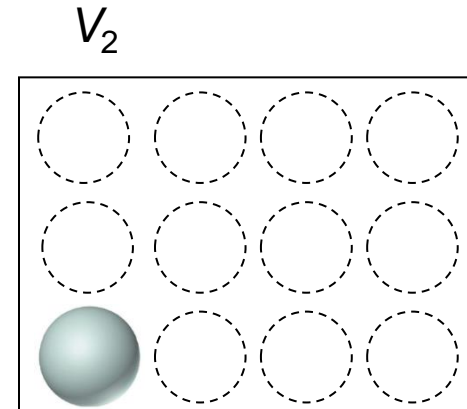
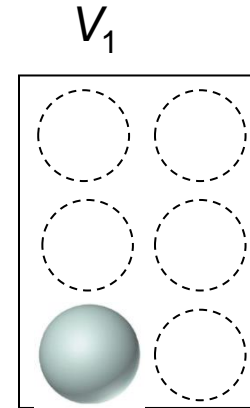
## $\Delta S$ of a single ideal gas molecule

$$S = k_B \ln \Omega$$

$$V_1 \rightarrow V_2$$

$$\Delta S = k_B \{ \ln \Omega_2 - \ln \Omega_1 \}$$

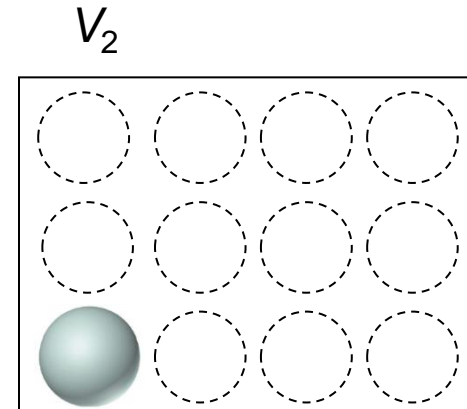
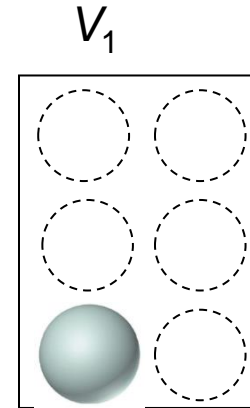
$$\Delta S = k_B \ln \frac{\Omega_2}{\Omega_1}$$



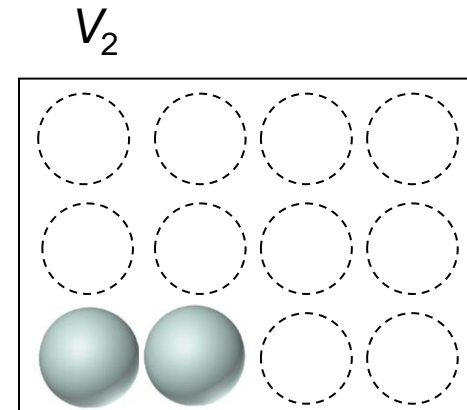
# $\Delta S$ of a single ideal gas molecule

$$\frac{\Omega_2}{\Omega_1} = \frac{V_2}{V_1}$$

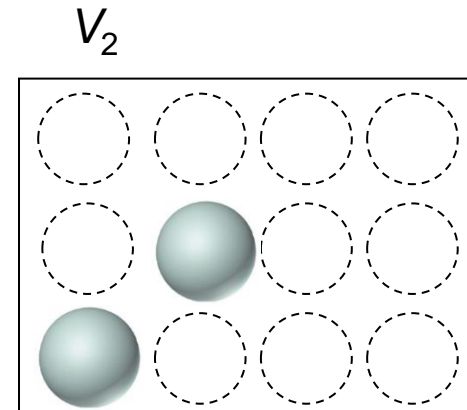
$$\Delta S = k_B \ln \frac{V_2}{V_1}$$



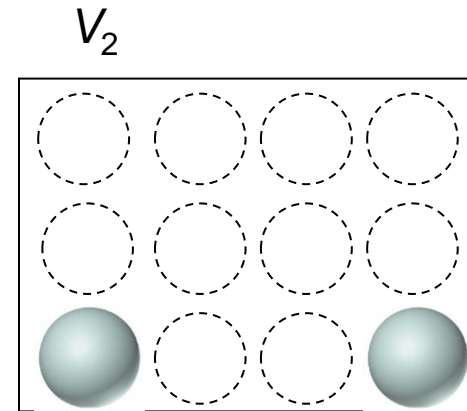
# $\Delta S$ of two ideal gas molecules



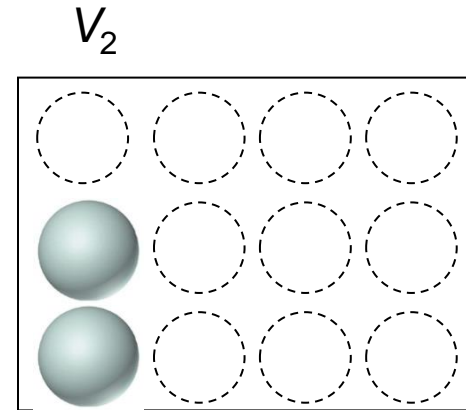
# $\Delta S$ of two ideal gas molecules



# $\Delta S$ of two ideal gas molecules

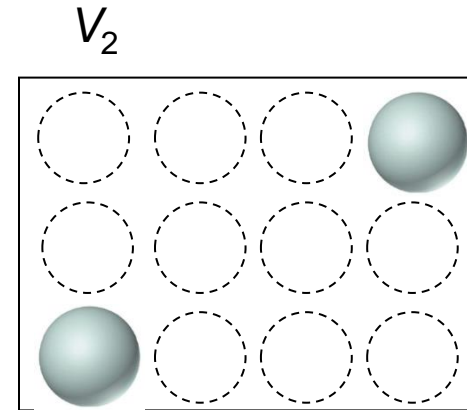


# $\Delta S$ of two ideal gas molecules

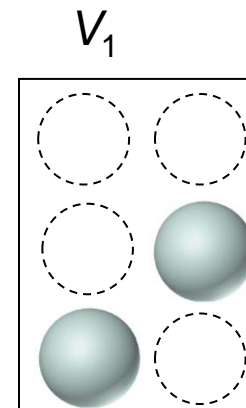


# $\Delta S$ of two ideal gas molecules

$$\Omega_2 \Rightarrow V_2 \times V_2$$

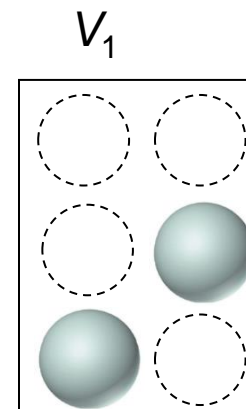
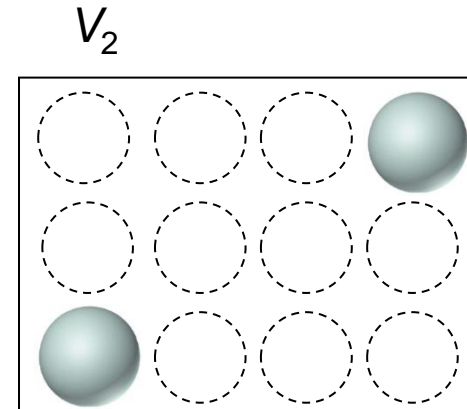


$$\Omega_1 \Rightarrow V_1 \times V_1$$



$\Delta S$  of two ideal gas molecules

$$\frac{\Omega_2}{\Omega_1} = \left( \frac{V_2}{V_1} \right)^2$$





$\Delta S$  of  $n$  moles of ideal gas molecules

$$\frac{\Omega_2}{\Omega_1} = \left( \frac{V_2}{V_1} \right)^{nN_A} \qquad \Delta S = k_B \ln \frac{\Omega_2}{\Omega_1}$$

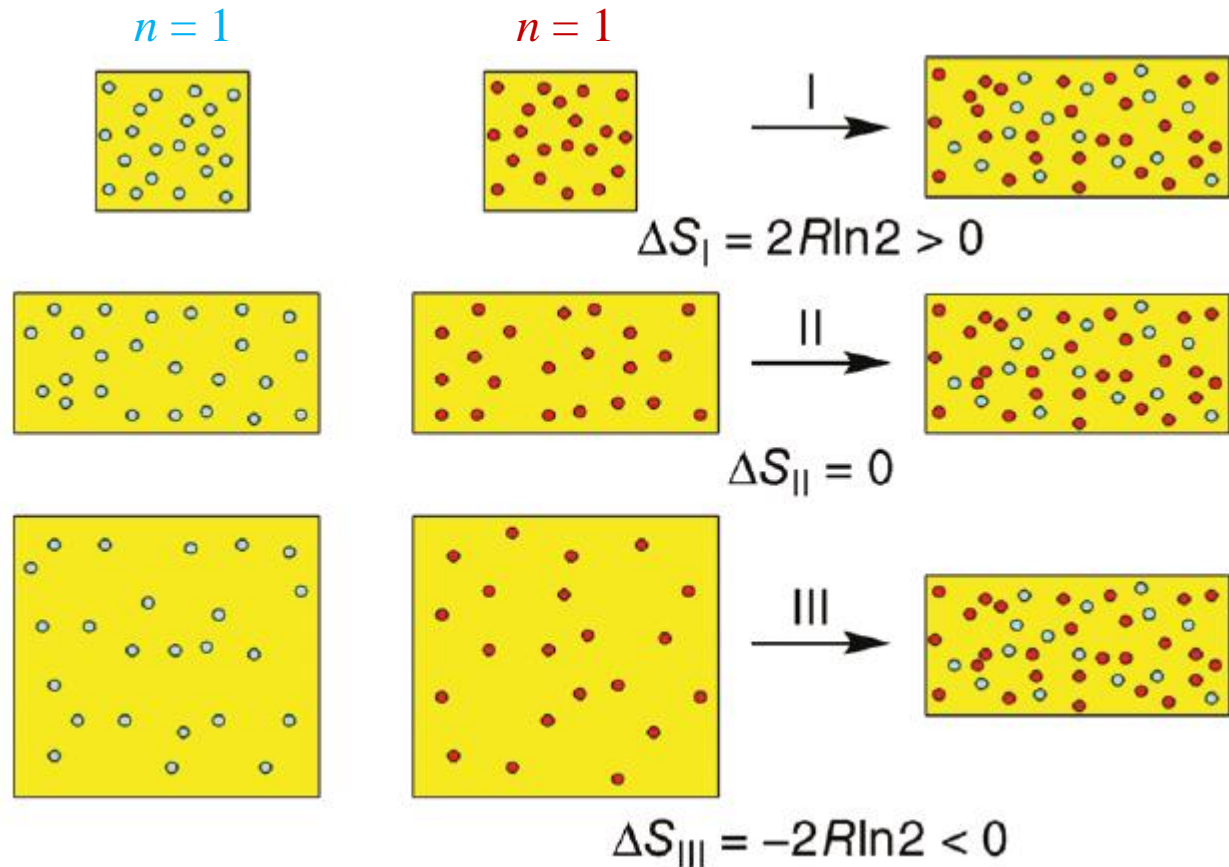
$$\Delta S = nN_A k_B \ln \frac{V_2}{V_1}$$

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

$R$ : Gas constant  
 $8.314 \text{ JK}^{-1}\text{mol}^{-1}$

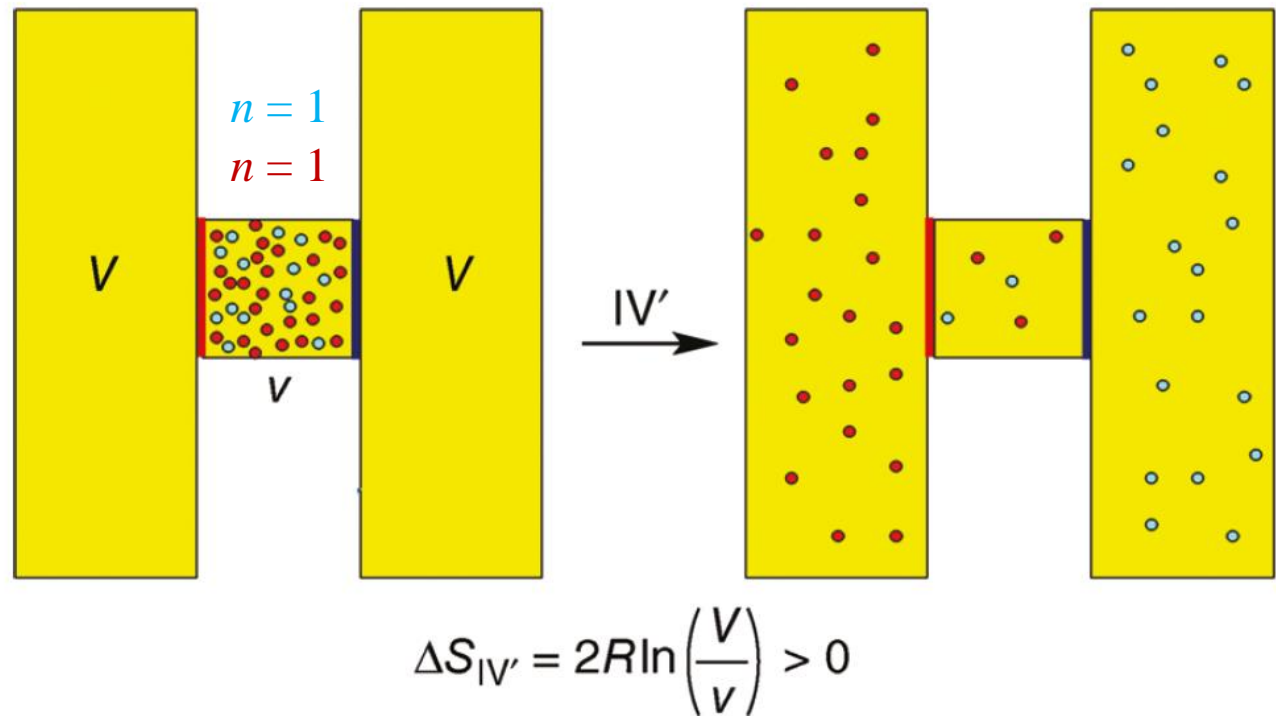
# Mixing May Not Lead to Larger Entropy

$$\Delta S = nR \ln \frac{V_2}{V_1}$$



# Demixing May Not Lead to Smaller Entropy

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

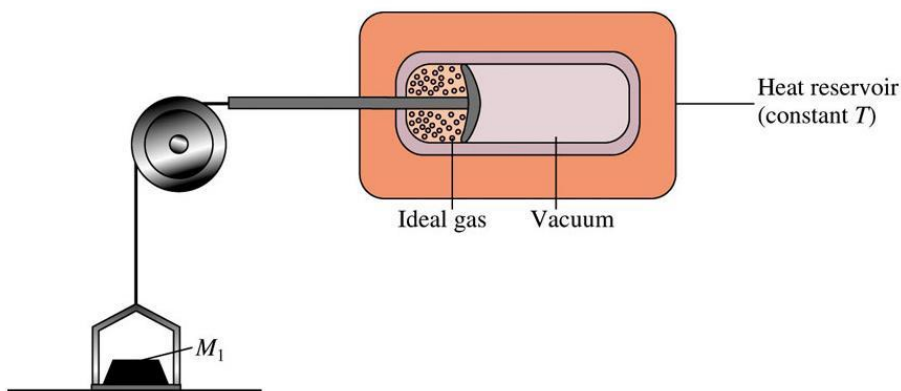


# Heat Change of a Reversible Isothermal Process

$$w = -\sum_{i=1}^{\infty} P_i \Delta V_i$$

$$w = -\int_V^{V'} P_{\text{ext}} dV \quad P_{\text{ext}} \approx P = \frac{nRT}{V} \quad \text{For ideal gas only}$$

$$q_{\text{rev}} = nRT \ln \left( \frac{V_2}{V_1} \right)$$



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For an isothermal process

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

$$q_{rev} = nRT \ln \left( \frac{V_2}{V_1} \right)$$

$$\therefore \Delta S = \frac{q_{rev}}{T}$$

The pathway under  
**reversible/equilibrium** conditions!

Sign of  $\Delta S$  determined by  
the heat flow direction.

**Unit of  $S$  is J/K**

# Second Law of Thermodynamics

Energy **spontaneously** tends to flow only from being concentrated in one place to becoming diffused or dispersed and spread out.

For any **spontaneous** process, the **entropy** of the universe must be increasing!

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} > 0$$

**Spontaneous** process – a process occurring on its own and requires no outside help.

# Second Law of Thermodynamics

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} > 0$$

☆ A quick analysis

$\Delta S_{sys}$	$\Delta S_{surr}$	$\Delta S_{univ}$	
+	+	+	Spontaneous
-	-	-	Non-spontaneous
+	-	?	Depends on the relative size
-	+	?	

# Total Entropy Change for Reversible Processes

Under equilibrium conditions:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T}$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}}$$

Surrounding's point of view

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0$$

because  $T = T_{\text{surr}}$  at equilibrium!



# Entropy of the Surrounding for Irreversible Processes

By definition, the surrounding has constant  $P$ ,  $V$ ,  $T$ , *etc.*

That is, the heat exchange in the surrounding occurs under *equilibrium conditions*:

$$\Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}}$$

$\Delta S_{\text{surr}}$  is primarily determined by the heat flow to or from the system.

$q < 0$ : system  $\rightarrow$  surrounding  $\Rightarrow S_{\text{surr}}$  increases

$q > 0$ : system  $\leftarrow$  surrounding  $\Rightarrow S_{\text{surr}}$  decreases

# Second Law of Thermodynamics

*Heat is not observed to pass spontaneously from a body at **low**  $T$  to a body at **higher**  $T$ .*

Because  $\Delta S$  is path independent, we can consider a reversible process without losing generality:

$$\Delta S = \frac{q_{rev}}{T}$$

For the same amount of heat:

**Low**  $T \rightarrow$  larger  $\Delta S$

**High**  $T \rightarrow$  smaller  $\Delta S$

Heat flow: **Low**  $T \rightarrow$  **High**  $T$

$\Delta S - \Delta S < 0$

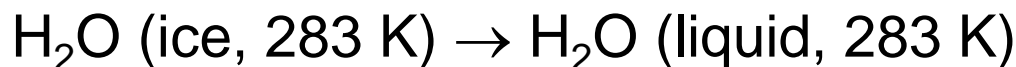


## Learning Check

Calculate the entropy change of the universe when an ice cube is melted at 10°C.

$$\Delta S (\text{melting, 273 K}) = 22.00 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H (\text{melting, 273 K}) = 6.006 \text{ kJ mol}^{-1}$$



$$\begin{aligned}\Delta S_{\text{universe}} &= \Delta S_{\text{system}} - \frac{\Delta H}{T_{\text{surr}}} \\ &= 22.00 - 6006 / 283 = 0.78 \text{ JK}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\Delta S_{\text{universe}} > 0 \quad \text{Spontaneous!}$$