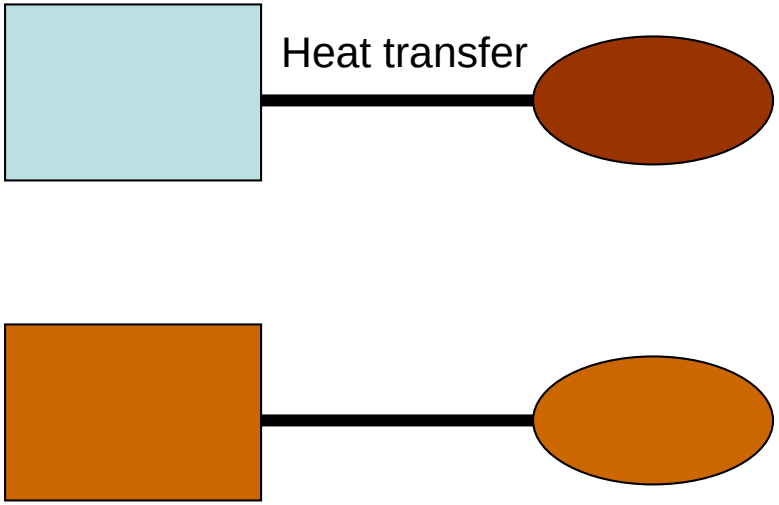
Chapter 19
Chemical Thermodynamics

Zeroth Law of Thermodynamics



Thermal Equilibrium

Same Temperature

Equilibrium – unchanged with time

First Law of Thermodynamics

E (system) + *E* (surrounding) = constant

$$\Delta E = q + w$$

TABLE 5.1 • Sign Conventions for *q*, *w*, and ΔE

For *q*	+ means system *gains* heat	− means system *loses* heat
For *w*	+ means work done *on* system	− means work done *by* system
For ΔE	+ means *net gain* of energy by system	− means *net loss* of energy by system

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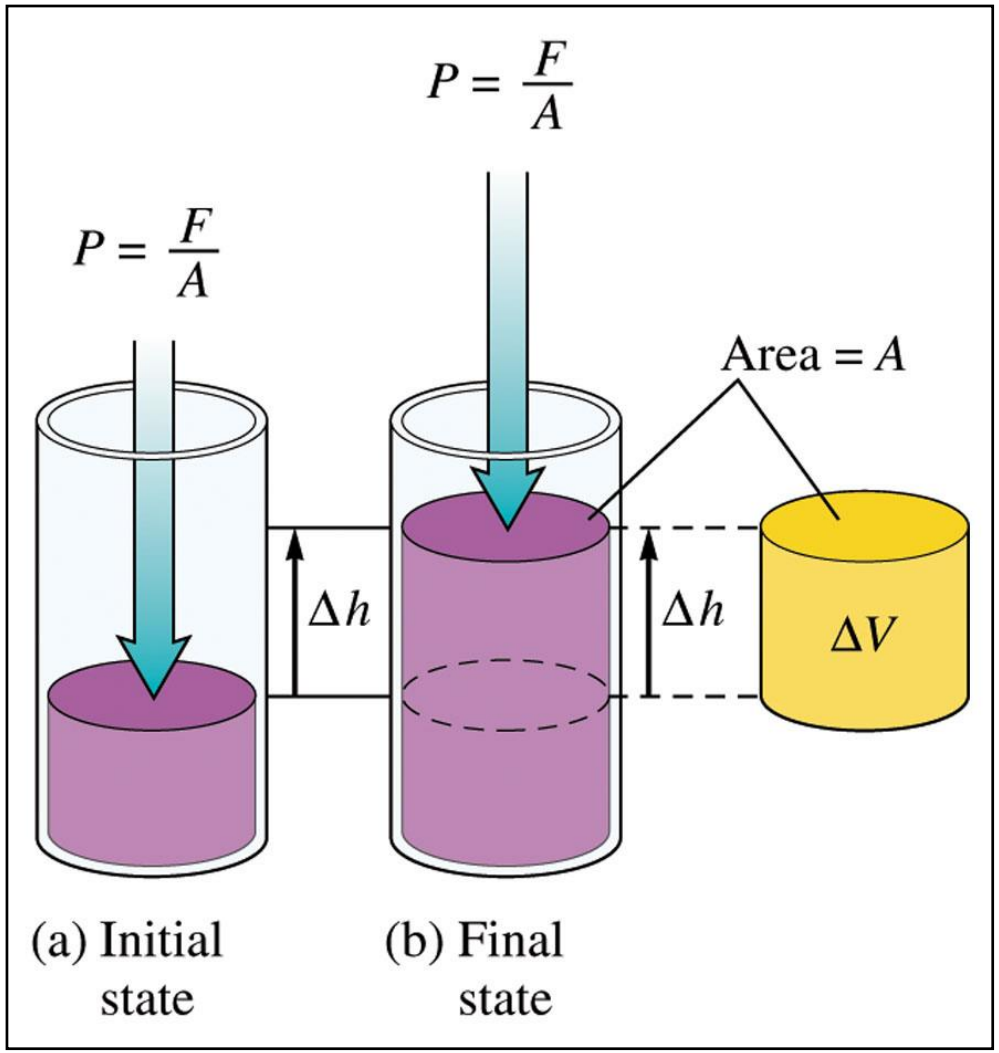
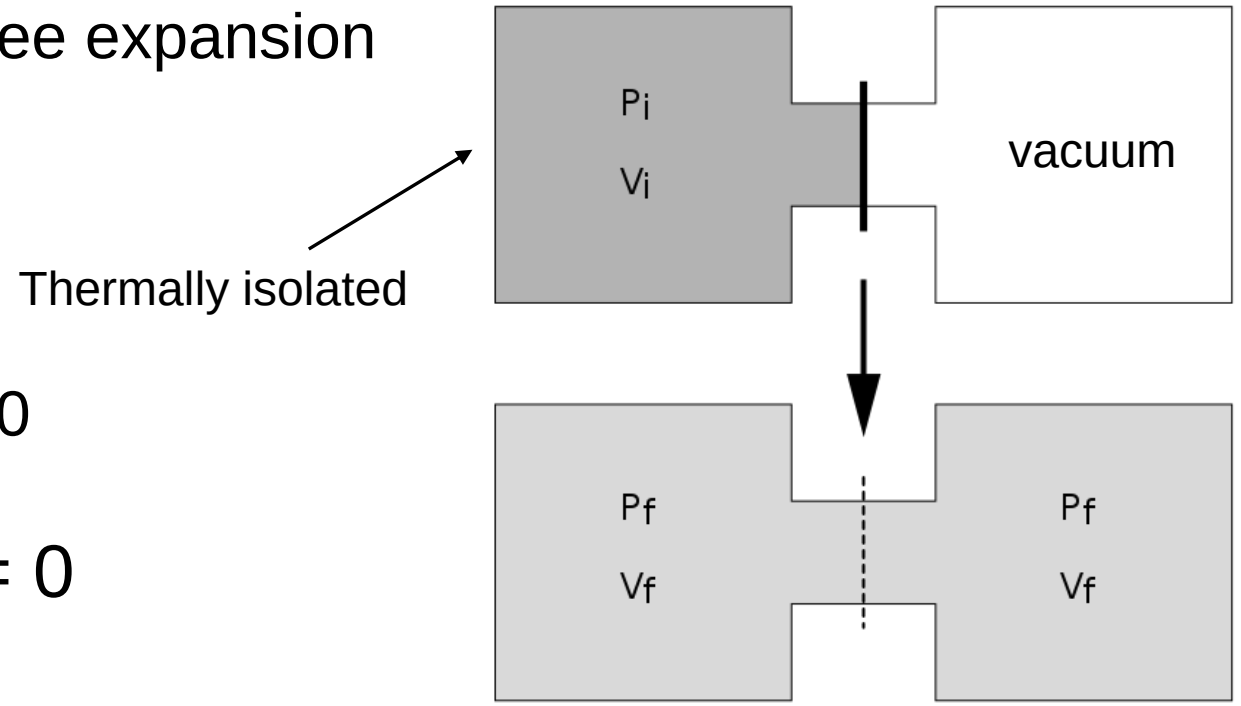
$$w = -P_{\text{ext}}\Delta V$$



Driving Force of a Process

Case study 1: Free expansion



$q = 0$

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

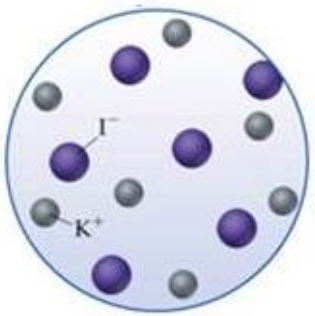
$\Delta E = q + w = 0$

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

Driving Force of a Process

Case study 2: Dissolution

$KI(s) \rightarrow K^+(aq) + I^-(aq) \quad \Delta H = +21$ kJ/mol



Weak hydration energy

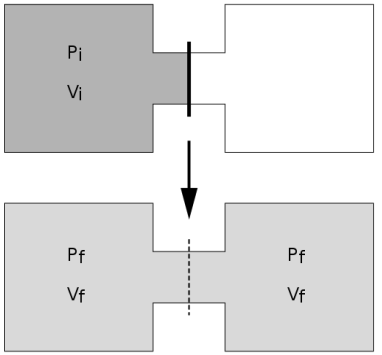
Case study 3: Melting

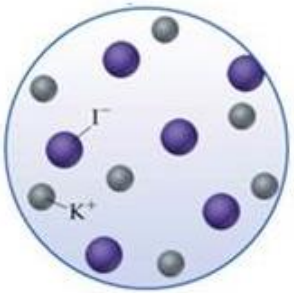
These are spontaneous processes but $\Delta E > 0$!

Driving Force of a Process

What's in common?

Increase in randomness or disorder

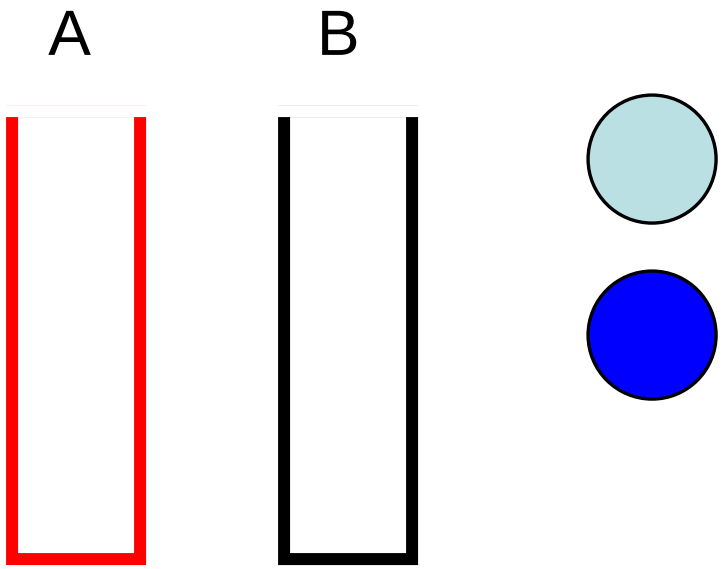




Likeliness

Balls in a container

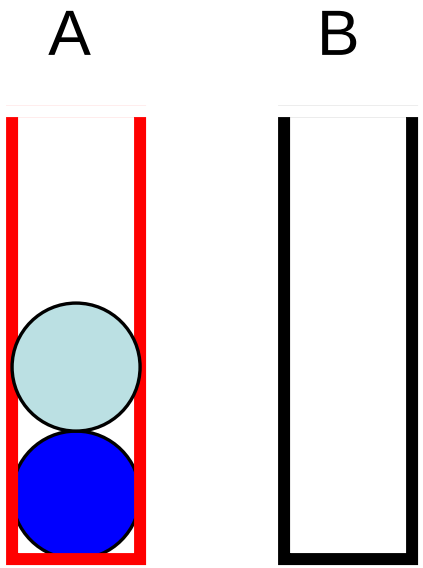
	# of ways
Both in A	
Both in B	
Each has one	



Likeliness

Balls in a container

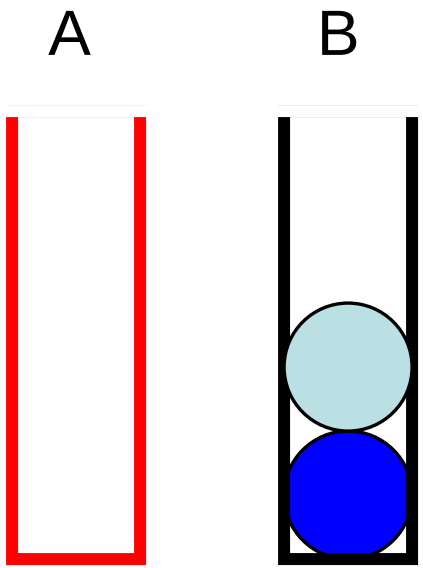
	# of ways
Both in A	1
Both in B	
Each has one	



Likeliness

Balls in a container

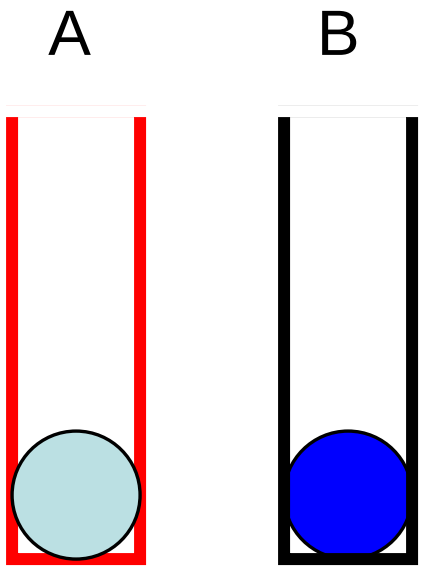
	# of ways
Both in A	1
Both in B	1
Each has one	



Likeliness

Balls in a container

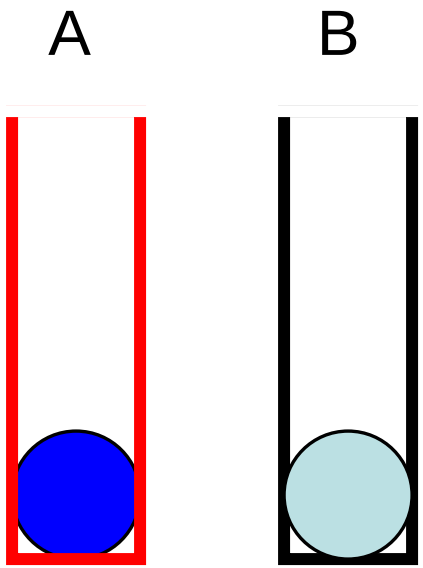
	# of ways
Both in A	1
Both in B	1
Each has one	1



Likeliness

Balls in a container

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



Likeliness

Balls in a container

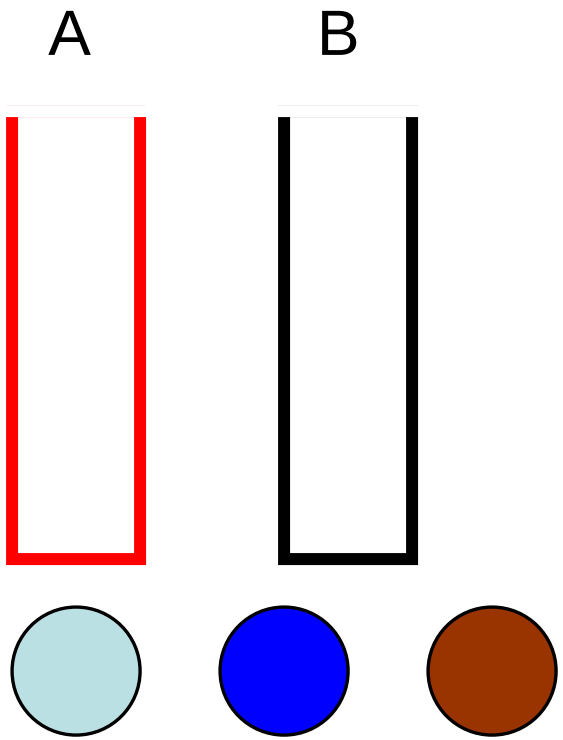
# of ways

All in A

All in B

2 in A, 1 in B

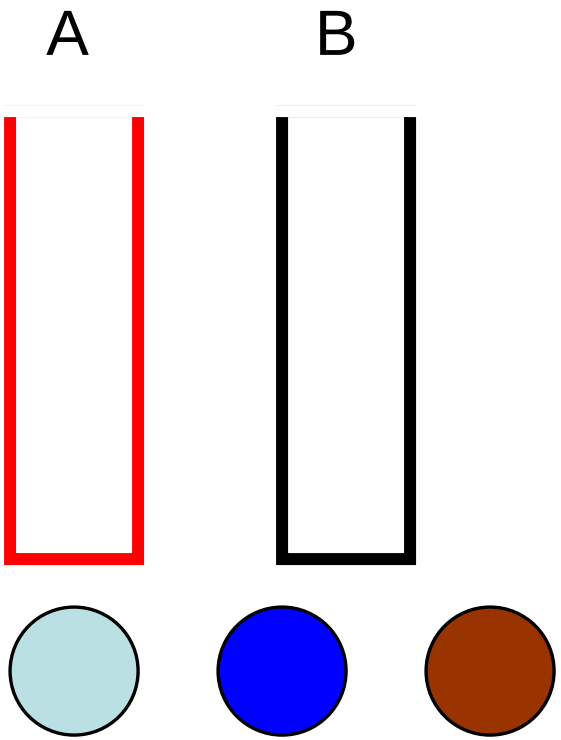
2 in B, 1 in A



Likeliness

Balls in a container

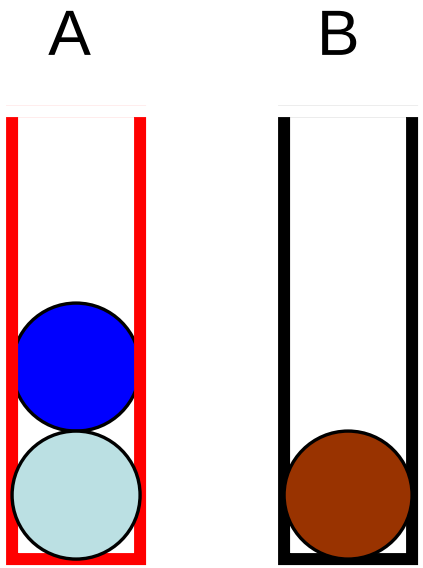
	# of ways
All in A	1
All in B	1
2 in A, 1 in B	
2 in B, 1 in A	



Likeliness

Balls in a container

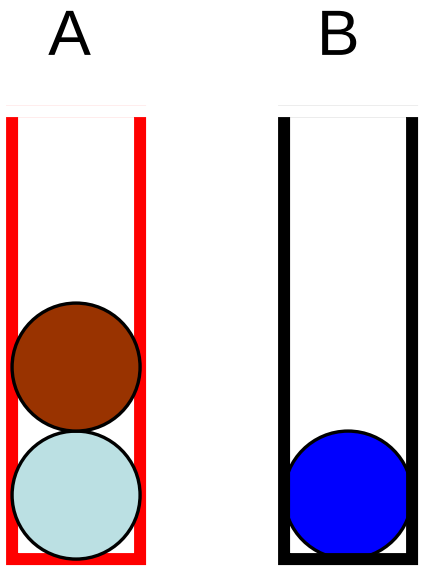
	# of ways
All in A	1
All in B	1
2 in A, 1 in B	1
2 in B, 1 in A	



Likeliness

Balls in a container

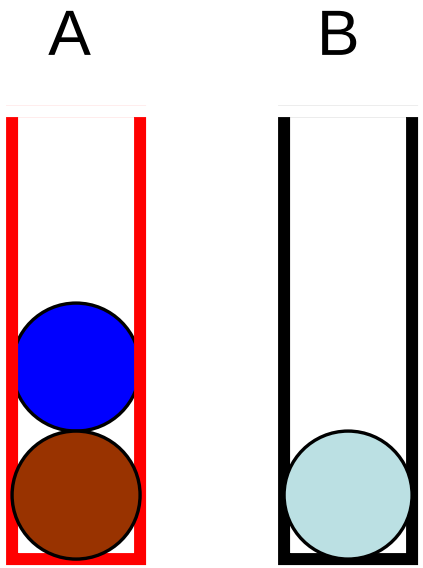
	# of ways
All in A	1
All in B	1
2 in A, 1 in B	2
2 in B, 1 in A	



Likeliness

Balls in a container

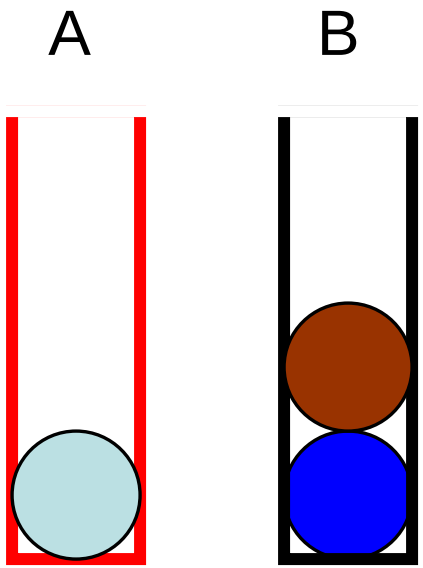
	# of ways
All in A	1
All in B	1
2 in A, 1 in B	3
2 in B, 1 in A	



Likeliness

Balls in a container

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



Likeliness

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

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

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

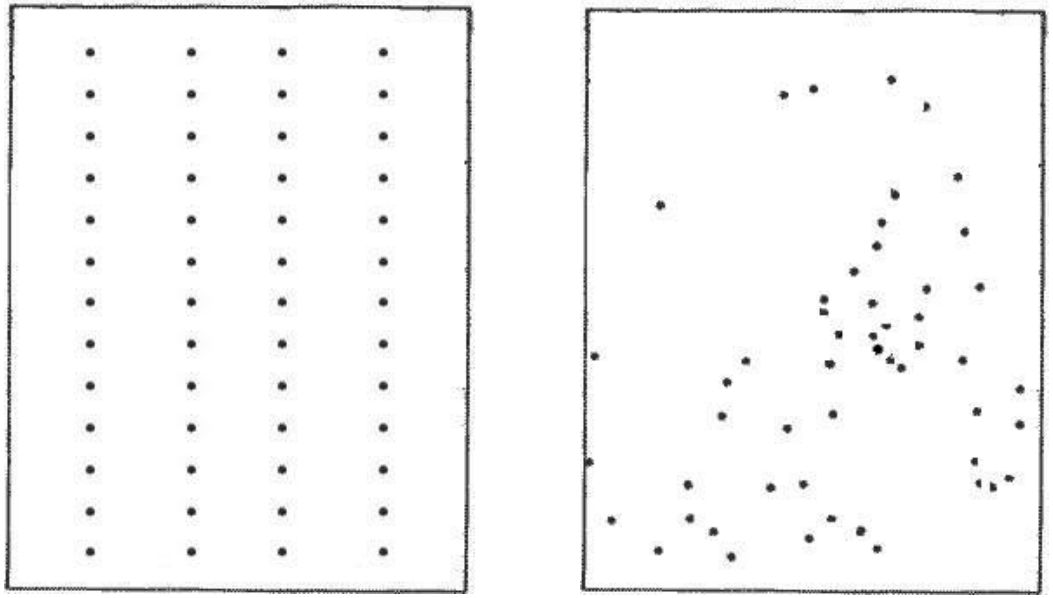
Randomly place one mole of molecules in two containers

	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!

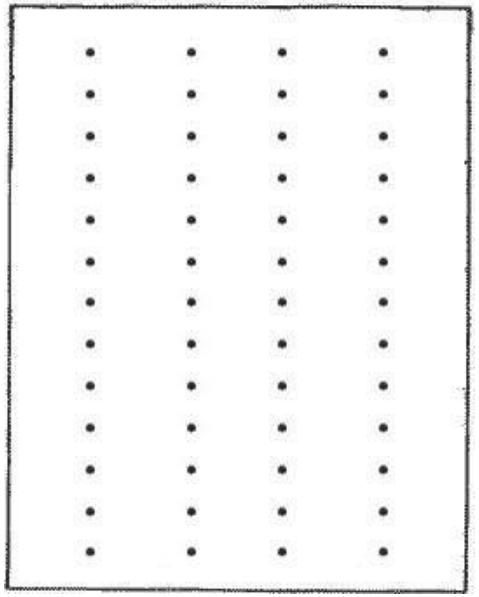
States of greater disorder are favored over more ordered states!

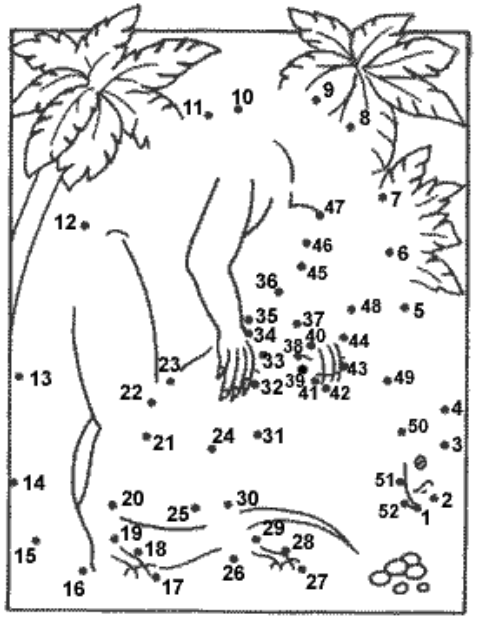
Order or Disorder ?



States of greater disorder are favored over more ordered states!

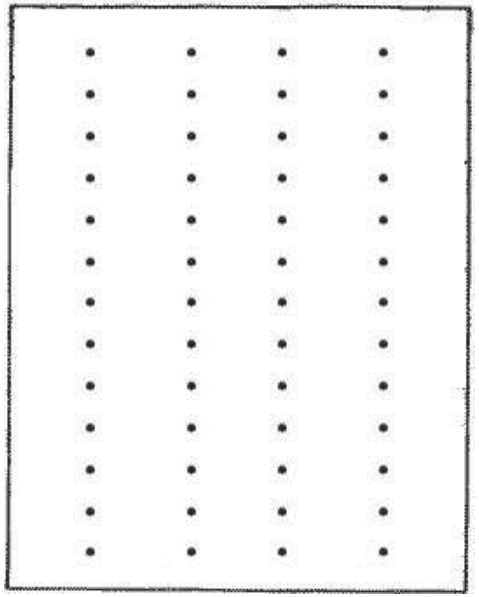
Order or Disorder ?

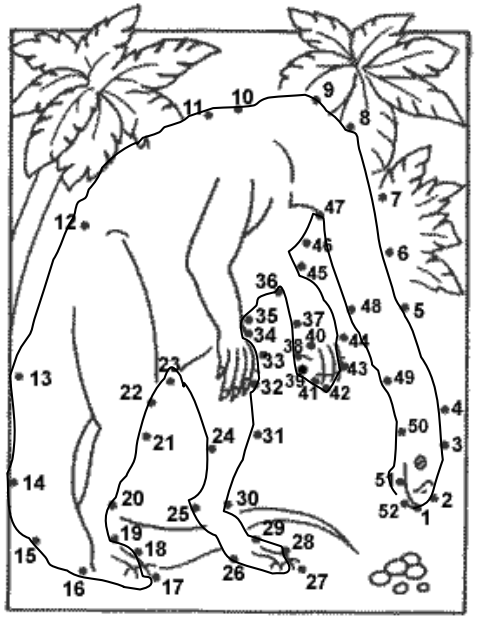




States of greater disorder are favored over more ordered states!

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!

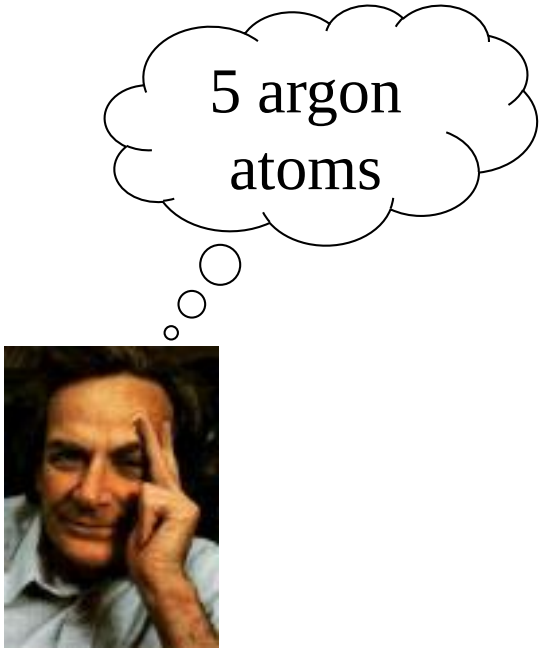
Learning Check

Which one of the following has the largest disorder?

1. Five atoms of Argon

2. One molecule of CH_4

3. Two molecules of oxygen



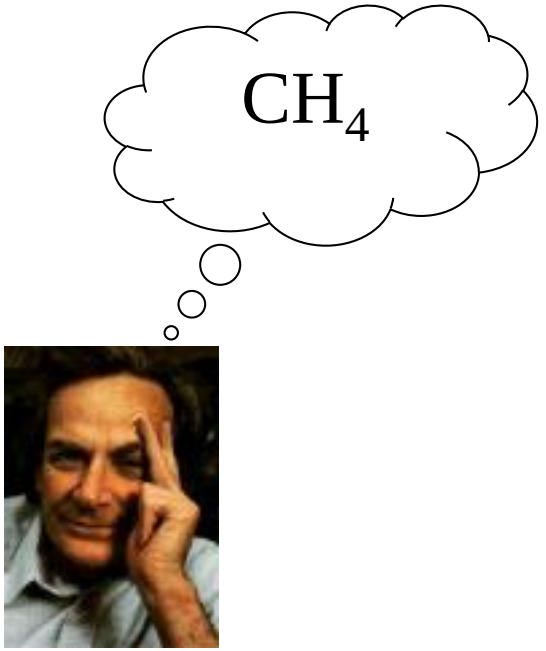
Learning Check

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

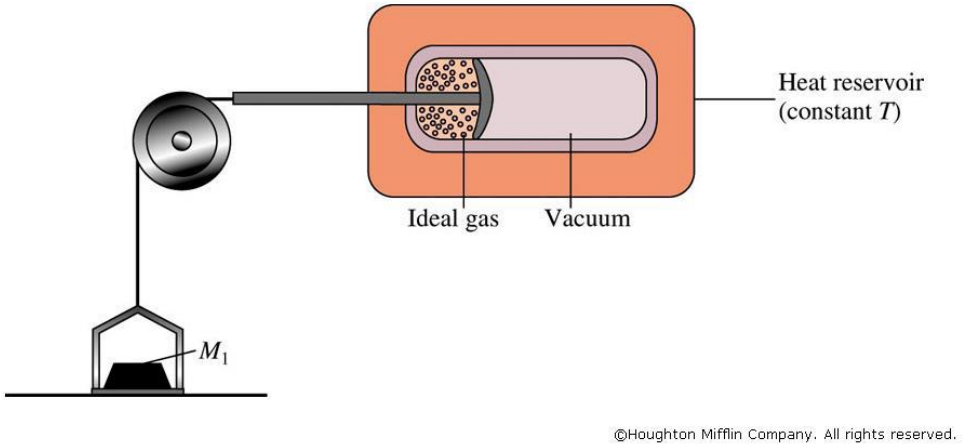
$$PV = nRT$$

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

$M_1 \rightarrow M_1/4$

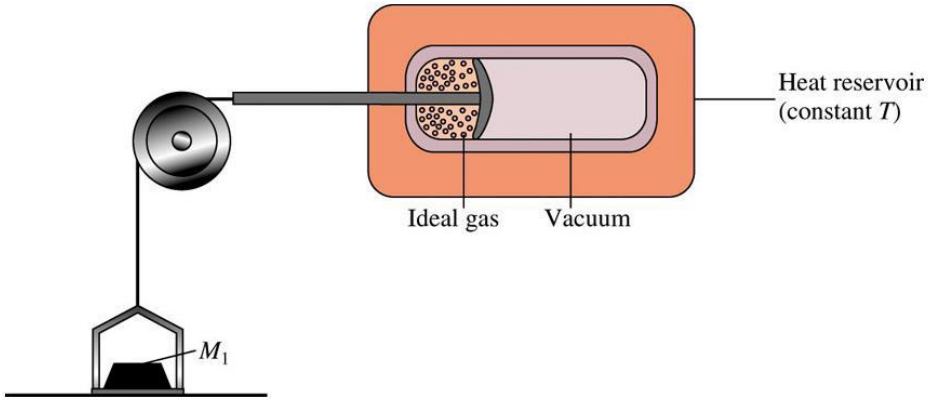
$$P_2 = \frac{P_1}{4} \quad \Rightarrow \quad V_2 = 4V_1 \quad \Rightarrow \quad w = -\frac{P_1}{4}\left(4V_1 - V_1\right) = -\frac{3}{4}P_1V_1$$

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

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) $M_1 \rightarrow M_1/2$

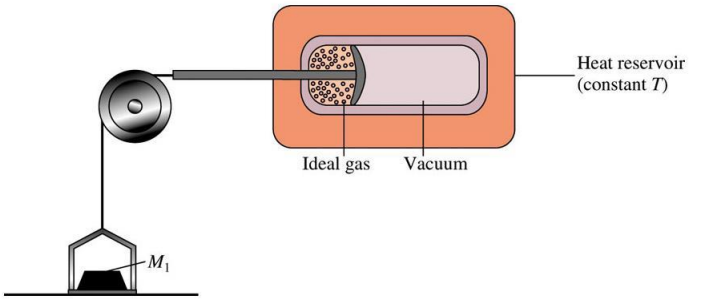
$$P_2 = \frac{P_1}{2} \Rightarrow V_2 = 2V_1 \Rightarrow w = -\left(\frac{P_1}{2}\right)\left(2V_1 - V_1\right) = -\frac{1}{2}P_1V_1$$

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

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

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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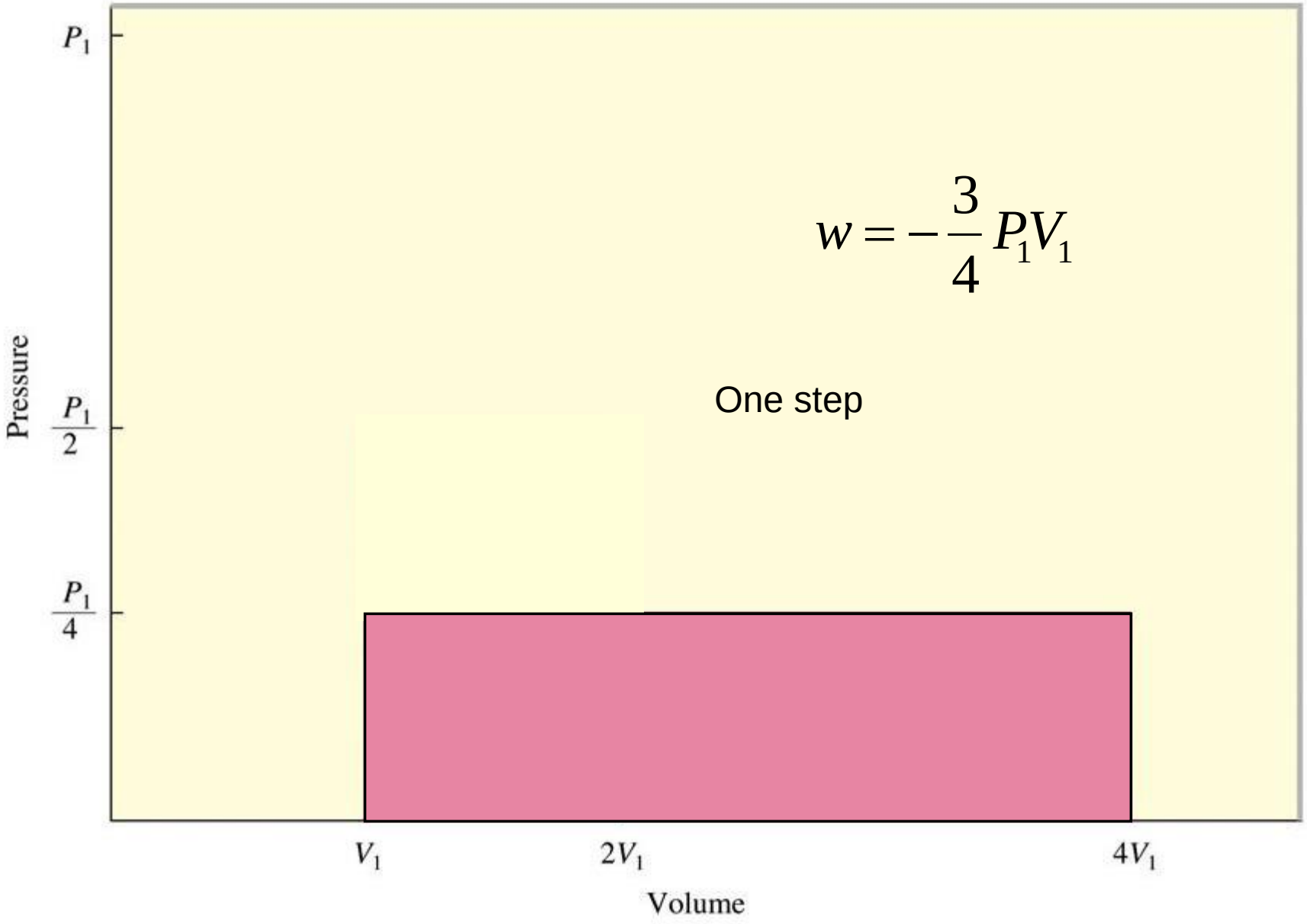
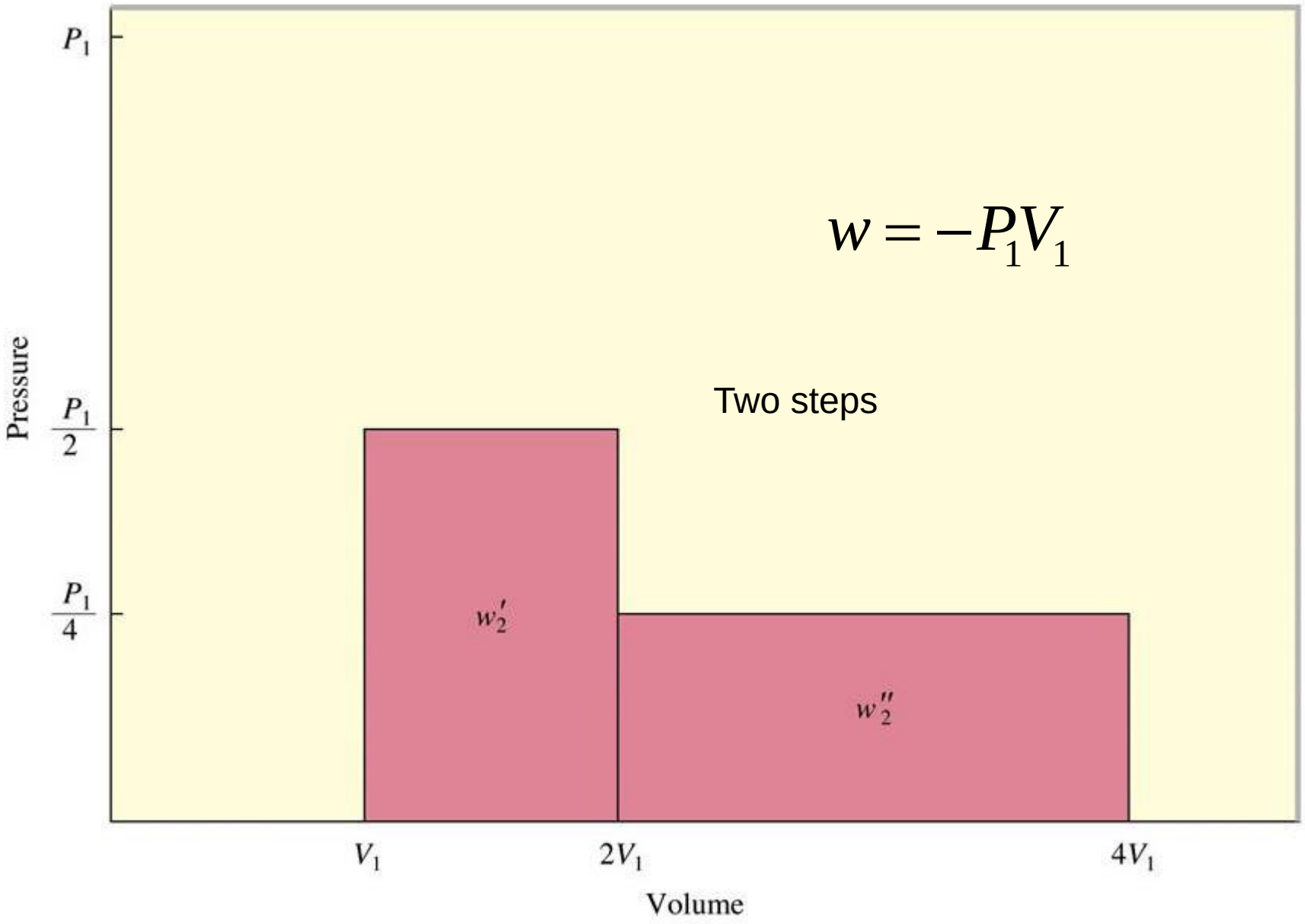


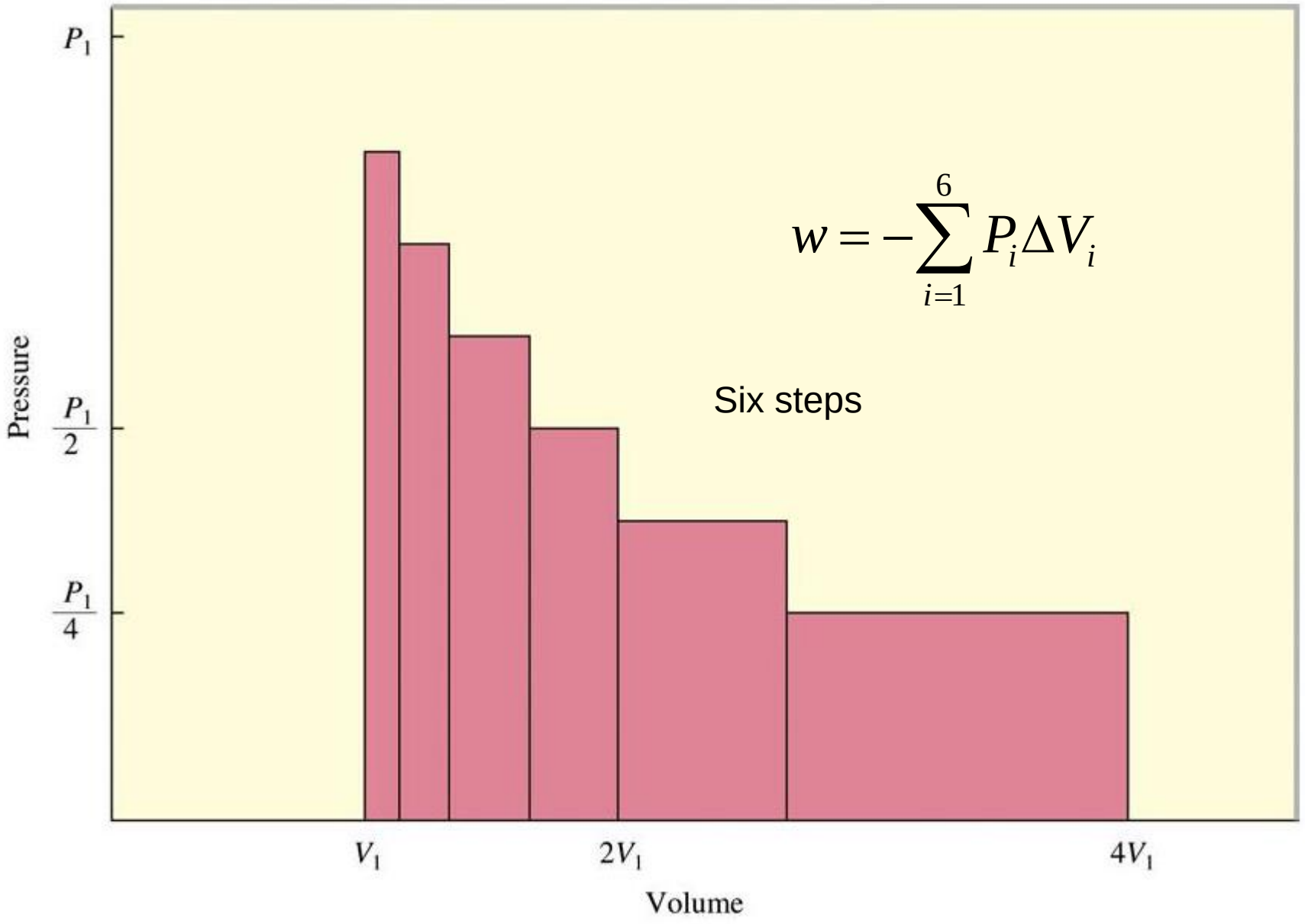
$$w = -\frac{3}{4} P_1 V_1$$

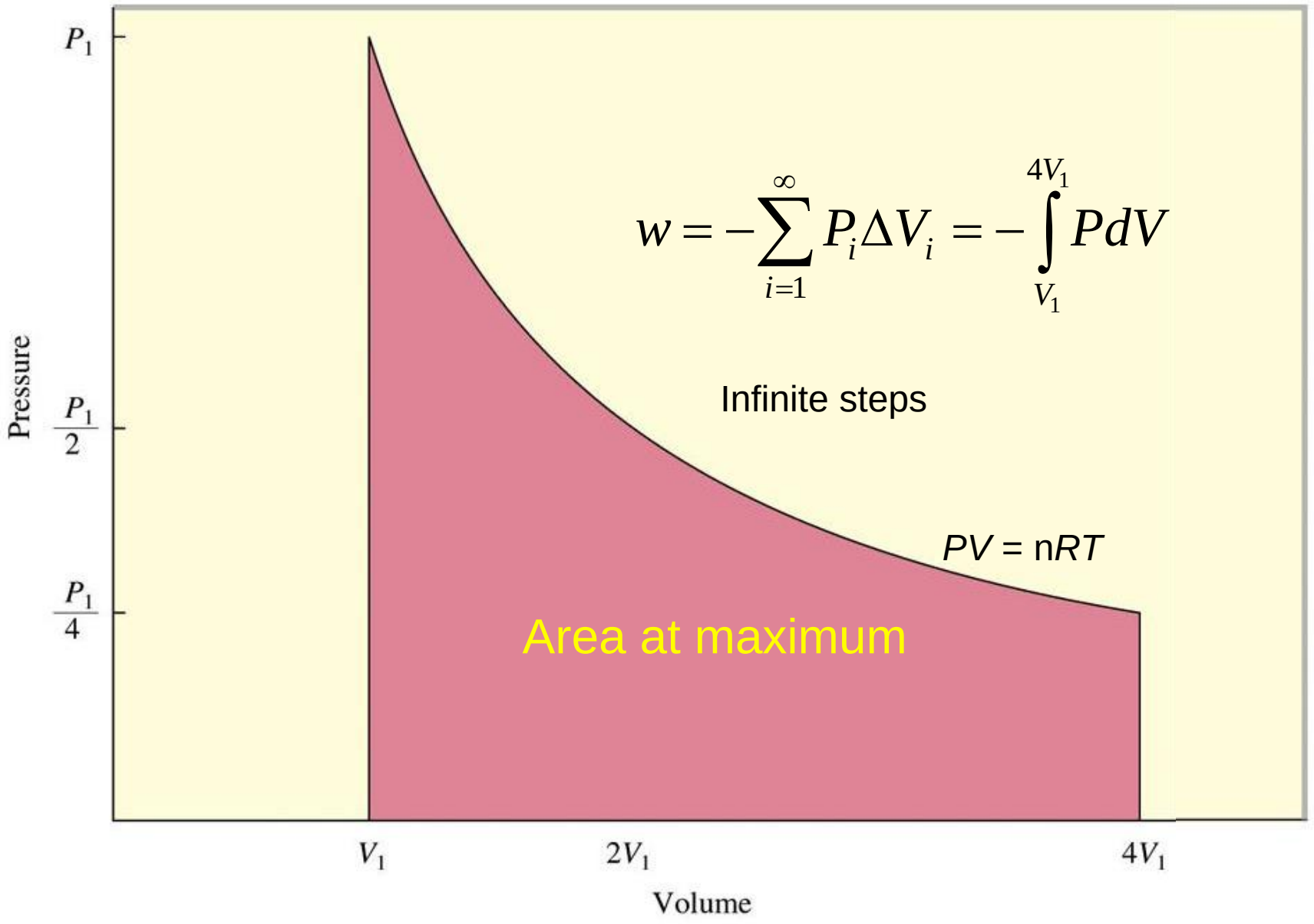
One step



$$w = -P_1 V_1$$

Two steps


P_1
$\frac{P_1}{2}$
$\frac{P_1}{4}$
Pressure
V_1
$2V_1$
$4V_1$
Volume
$w = -\sum_{i=1}^{6} P_i \Delta V_i$
Six steps


P_1
$\frac{P_1}{2}$
$\frac{P_1}{4}$
Pressure
V_1
$2V_1$
$4V_1$
Volume
$w = -\sum_{i=1}^{\infty} P_i \Delta V_i = -\int_{V_1}^{4V_1} P dV$
Infinite steps
$PV = nRT$
Area at maximum

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 ($P_{system} = P_{ext}$)

Real-life examples:

Water boiling; ice melting

Coexistence → 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	$-1.16P_1V_1$
	∞	$-1.4P_1V_1$

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

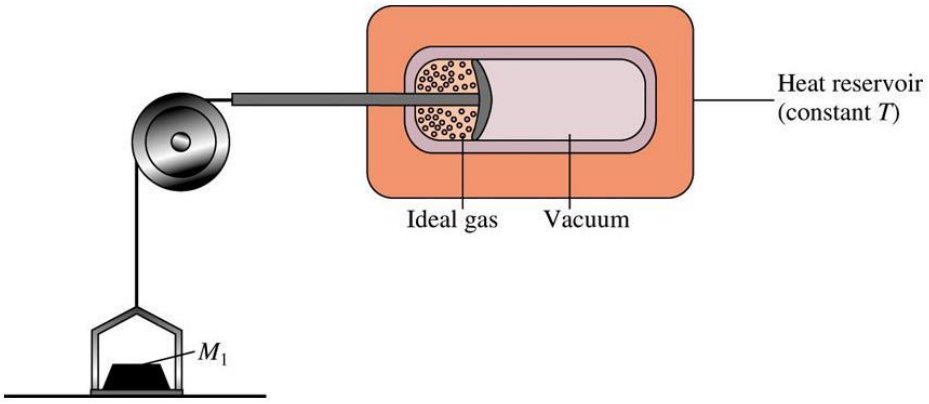
$$w = -\sum_{i=1}^{\infty} P_i \Delta V_i$$

$$w = -\int_{V_0}^{V_f} P_{ext}\, dV \qquad P_{ext} = P = \frac{nRT}{V}$$ 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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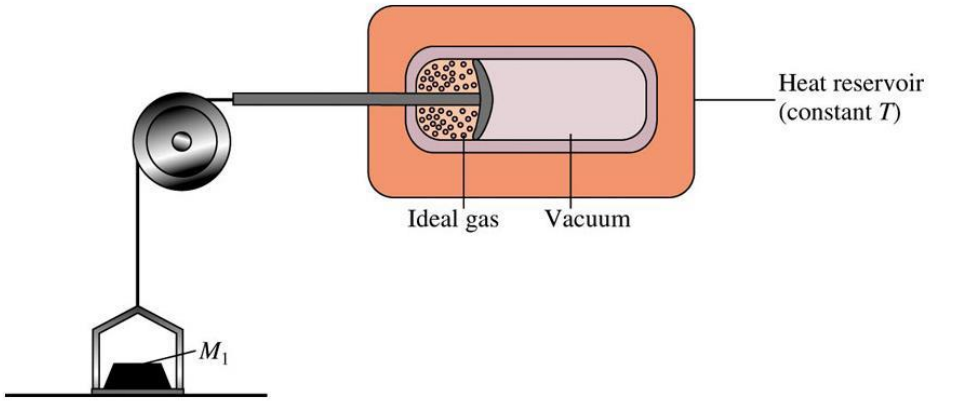
Isothermal Compression of an Ideal Gas

$M_1/4 \rightarrow M_1$

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

$$w = -P_1\left(V_1 - 4V_1\right) = 3P_1V_1$$



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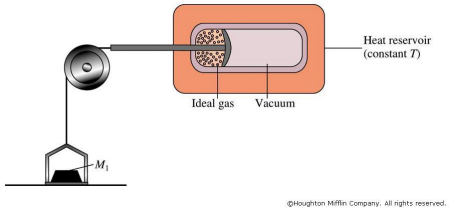
$M_1/4 \rightarrow M_1/2 \rightarrow M_1$

$$w = -\frac{P_1}{2}\left(2V_1 - 4V_1\right) - P_1\left(V_1 - 2V_1\right)$$
$$= 2P_1V_1$$

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	$-1.16P_1V_1$	$1.16P_1V_1$
	∞	$-1.4P_1V_1$	$1.4P_1V_1$
Compression (constant T)	1	$3P_1V_1$	$-3P_1V_1$
	2	$2P_1V_1$	$-2P_1V_1$
	4	$1.67P_1V_1$	$-1.67P_1V_1$
	∞	$1.4P_1V_1$	$-1.4P_1V_1$

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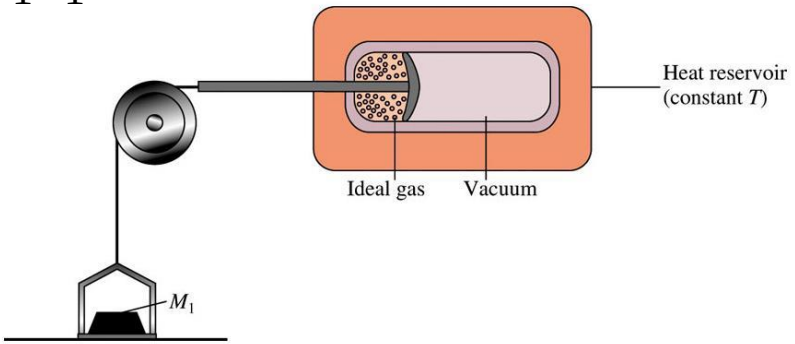
Isothermal Cyclic Expansion-Compression of an Ideal Gas

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: $w_{net} = -q_{net} = 2.25\ P_1V_1$

Two steps: $w_{net} = -q_{net} = P_1V_1$

Four steps: $w_{net} = -q_{net} = 0.51\ P_1V_1$

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

Path dependent, not a state function

The system is unchanged.

The surrounding has changed!

Isothermal Cyclic Expansion-Compression of an Ideal Gas

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

Reversible expansion and compression (system unchanged):

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

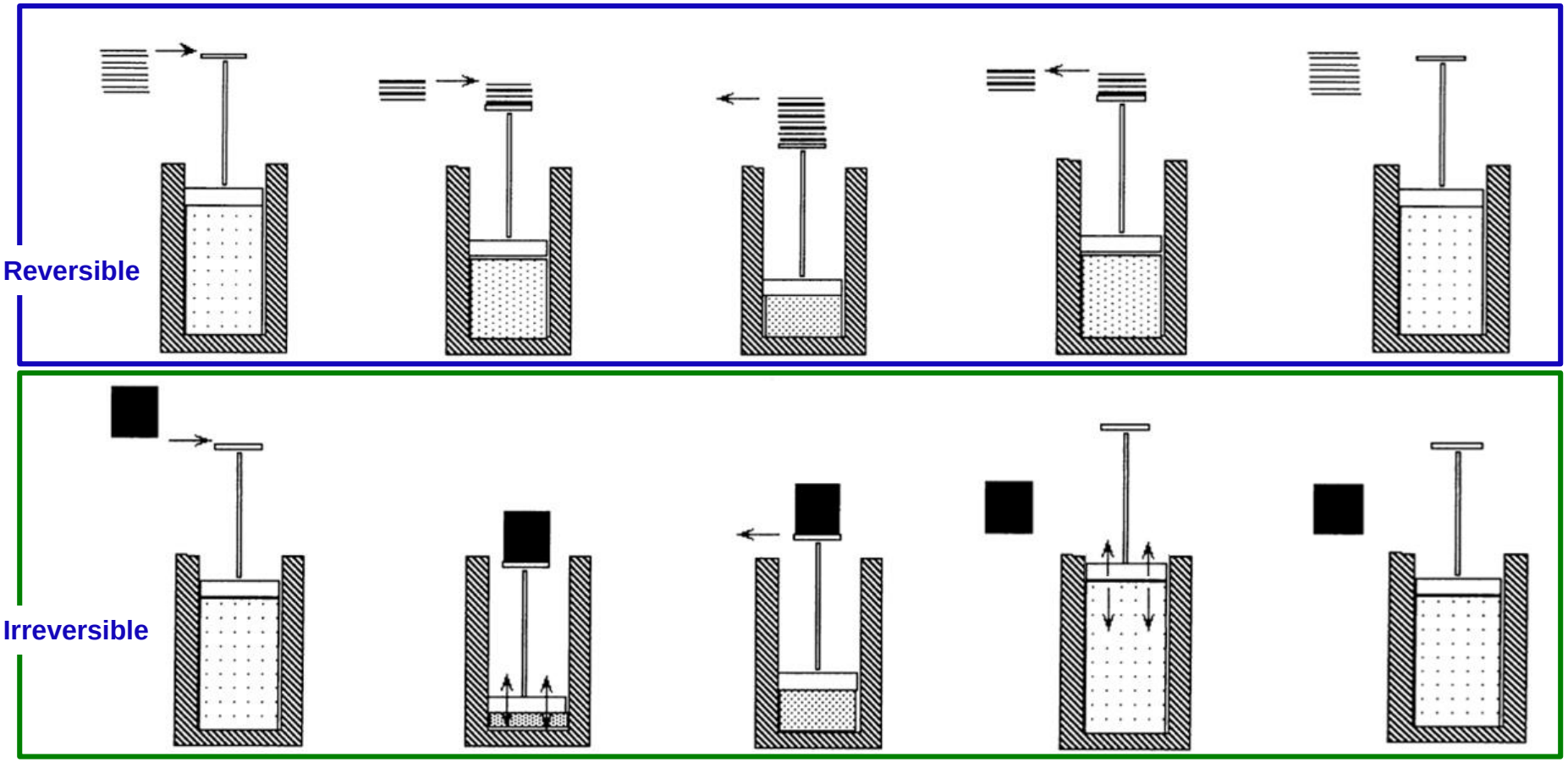
$$\therefore q_{\text{rev, net}} = +1.4P_1V_1 - 1.4P_1V_1 = 0$$

No net change after a cyclic path

⇨ q_{rev} and w_{rev} are state functions! – path is defined

Both the system and the surrounding are unchanged.

Isothermal Cyclic Expansion-Compression of an Ideal Gas



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: $w_{net} > 0$ $q_{net} < 0$

(Finite steps)

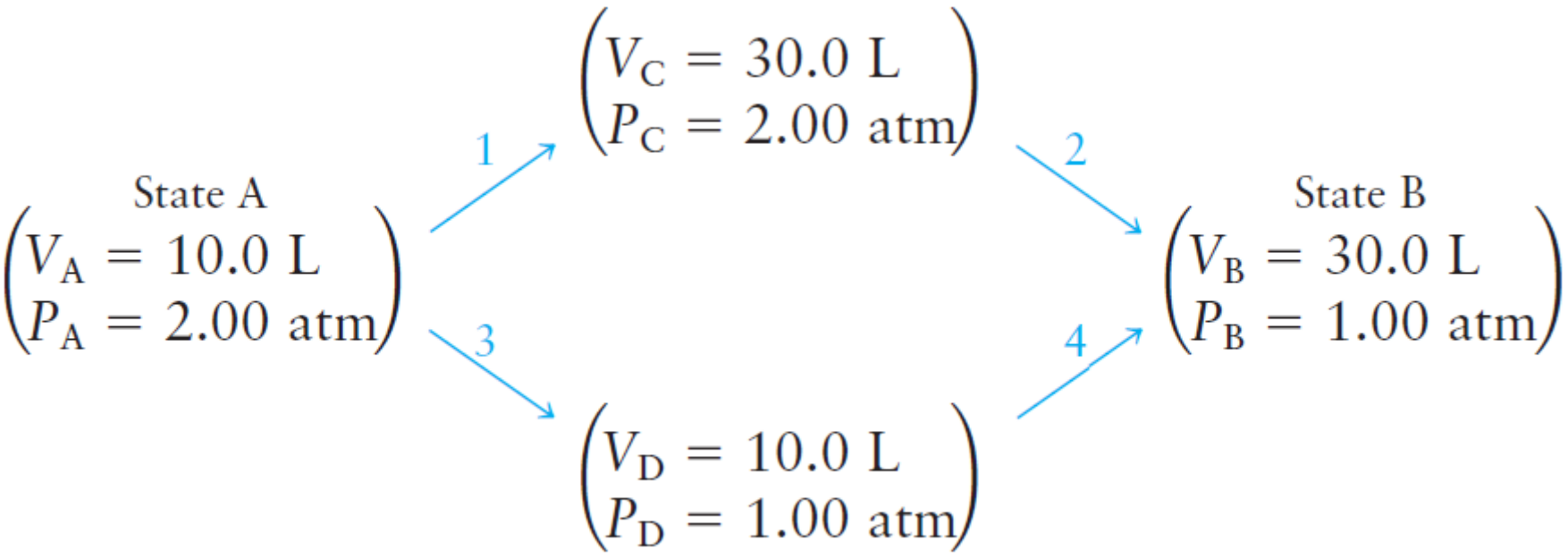
System is returned to the original condition but **NOT** the surrounding.

All real compression or expansion processes are thermodynamically irreversible!

(Energy distribution changed to a more disordered form)

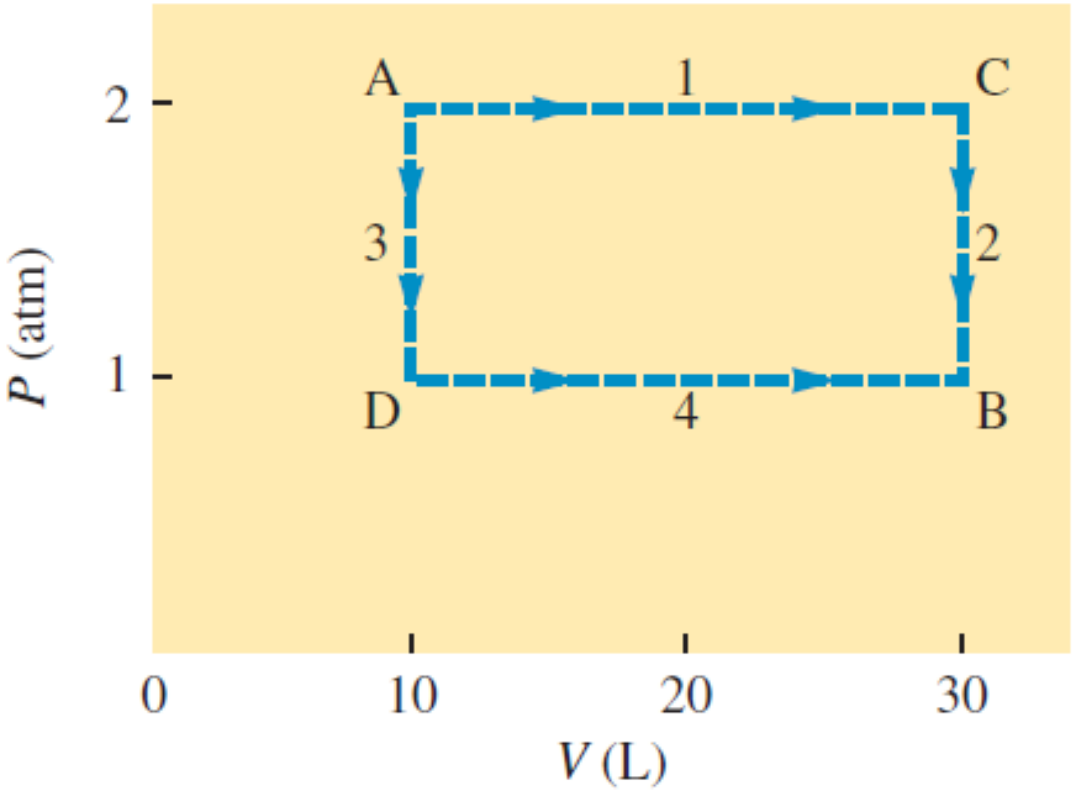
Energy, Enthalpy, Heat, and Work Under Different Conditions

- Consider 2.00 moles of a monatomic ideal gas that is taken from state A (P_A = 2.00 atm, V_A = 10.0 L) to state B (P_B = 1.00 atm, V_B = 30.0 L) by two different pathways:

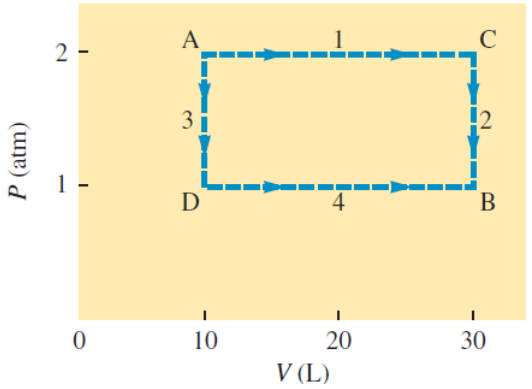


- Calculate q, w, ΔE, and ΔH for both pathways.

Energy, Enthalpy, Heat, and Work Under Different Conditions



Energy, Enthalpy, Heat, and Work Under Different Conditions



Step 1. State A to C: $P\Delta V = nR\Delta T$

$$P\Delta V = (2.00\ \text{atm})(20.0\ \text{L}) = 4.00 \times 10^1\ \text{L atm}$$

$$= 4.00 \times 10^1\ \text{L atm} \times \frac{101.3\ \text{J}}{\text{L atm}} = 4.05 \times 10^3\ \text{J}$$

$$\Delta T = \frac{P\Delta V}{nR} = \frac{4.05 \times 10^3\ \text{J}}{nR}$$

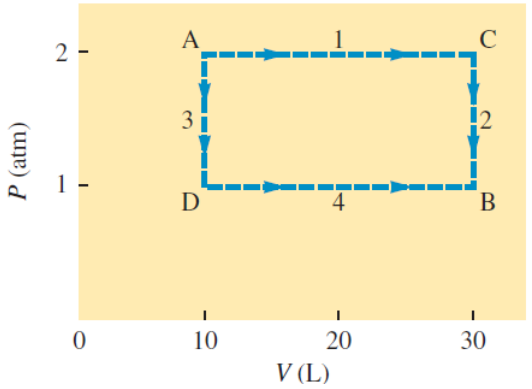
$$w_1 = -(2.00\ \text{atm})(30.0\ \text{L} - 10.0\ \text{L}) = -4.00 \times 10^1\ \text{L atm}$$

$$= -4.05 \times 10^3\ \text{J}$$

$$q_1 = q_p = nC_p\Delta T$$

$$= n\left(\frac{5}{2}R\right)\left(\frac{4.05 \times 10^3\ \text{J}}{nR}\right) = 1.01 \times 10^4\ \text{J}$$

Energy, Enthalpy, Heat, and Work Under Different Conditions



$$\Delta E_1 = nC_v\Delta T = n\left(\frac{3}{2}R\right)\left(\frac{4.05 \times 10^3\ \text{J}}{nR}\right) = 6.08 \times 10^3\ \text{J}$$

$$\Delta H_1 = nC_p\Delta T = n\left(\frac{5}{2}R\right)\left(\frac{4.05 \times 10^3\ \text{J}}{nR}\right) = 1.01 \times 10^4\ \text{J}$$

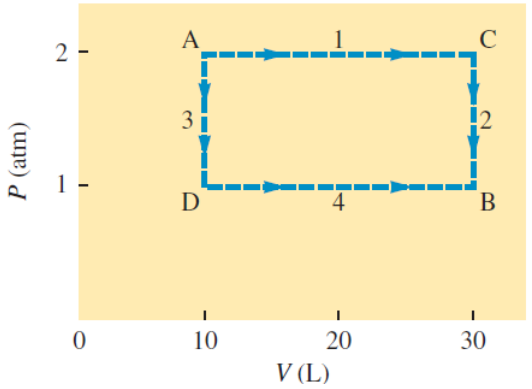
Step 2. State C to B:

$$\Delta PV = nR\Delta T$$

$$\Delta T = \frac{\Delta PV}{nR} = \frac{(1.00\ \text{atm} - 2.00\ \text{atm})(30.0\ \text{L})}{nR}$$

$$= \frac{-30.0\ \text{L atm}}{nR} = \frac{-3.04 \times 10^3\ \text{J}}{nR}$$

Energy, Enthalpy, Heat, and Work Under Different Conditions



$$q_2 = q_v = nC_v\Delta T = n\left(\frac{3}{2}R\right)\left(\frac{-3.04 \times 10^3\ \text{J}}{nR}\right)$$

$$= -4.56 \times 10^3\ \text{J}$$

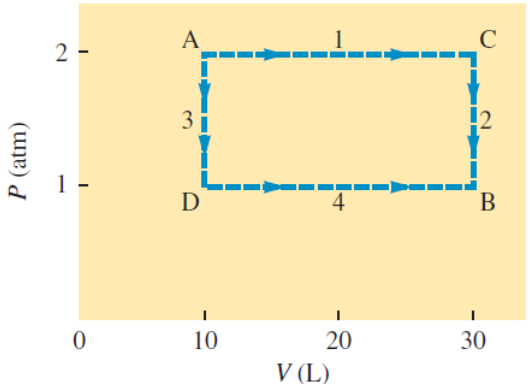
$$\Delta E_2 = nC_v\Delta T = n\left(\frac{3}{2}R\right)\left(\frac{-3.04 \times 10^3\ \text{J}}{nR}\right)$$

$$= -4.56 \times 10^3\ \text{J} = q_v$$

$$\Delta H_2 = nC_p\Delta T = n\left(\frac{5}{2}R\right)\left(\frac{-3.04 \times 10^3\ \text{J}}{nR}\right)$$

$$= -7.60 \times 10^3\ \text{J}$$

Energy, Enthalpy, Heat, and Work Under Different Conditions



Step 3. State A to D:

$$\Delta T = \frac{\Delta PV}{nR} = \frac{(-1.00\ \text{atm})(10.0\ \text{L})}{nR} = \frac{-10.0\ \text{L atm}}{nR} = \frac{-1.01 \times 10^3\ \text{J}}{nR}$$

$$w_3 = 0 \qquad (\Delta V = 0)$$

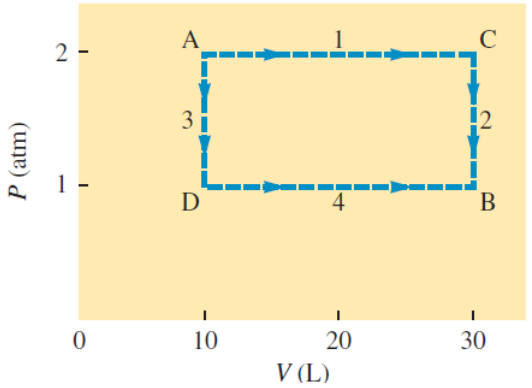
$$q_3 = q_v = nC_v\Delta T = n\left(\frac{3}{2}R\right)\left(\frac{-1.01 \times 10^3\ \text{J}}{nR}\right)$$

$$= -1.52 \times 10^3\ \text{J}$$

$$\Delta E_3 = q_v = -1.52 \times 10^3\ \text{J}$$

$$\Delta H_3 = nC_p\Delta T = n\left(\frac{5}{2}R\right)\left(\frac{-1.01 \times 10^3\ \text{J}}{nR}\right) = -2.53 \times 10^3\ \text{J}$$

Energy, Enthalpy, Heat, and Work Under Different Conditions



Step 4. State D to B:

$$\Delta T = \frac{P\Delta V}{nR} = \frac{(1.00\ \text{atm})(20.0\ \text{L})}{nR} = \frac{20.0\ \text{L atm}}{nR} = \frac{2.03 \times 10^3\ \text{J}}{nR}$$

$$w_4 = -P\Delta V = -(1.00\ \text{atm})(20.0\ \text{L}) = -20.0\ \text{L atm}$$

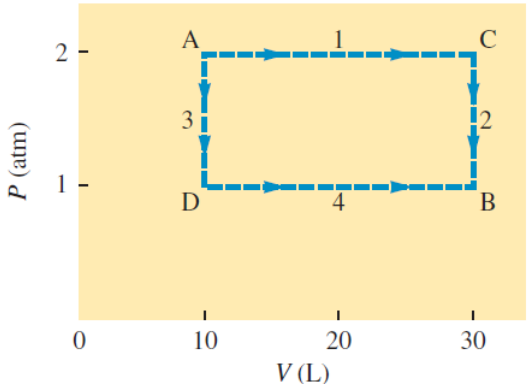
$$= -2.03 \times 10^3\ \text{J}$$

$$q_4 = q_p = nC_p\Delta T = n\left(\frac{5}{2}R\right)\left(\frac{2.03 \times 10^3\ \text{J}}{nR}\right) = 5.08 \times 10^3\ \text{J}$$

$$\Delta E_4 = nC_vT = n\left(\frac{3}{2}R\right)\left(\frac{2.03 \times 10^3\ \text{J}}{nR}\right) = 3.05 \times 10^3\ \text{J}$$

$$\Delta H_4 = nC_p\Delta T = n\left(\frac{5}{2}R\right)\left(\frac{2.03 \times 10^3\ \text{J}}{nR}\right) = 5.08 \times 10^3\ \text{J} = q_p$$

Energy, Enthalpy, Heat, and Work Under Different Conditions

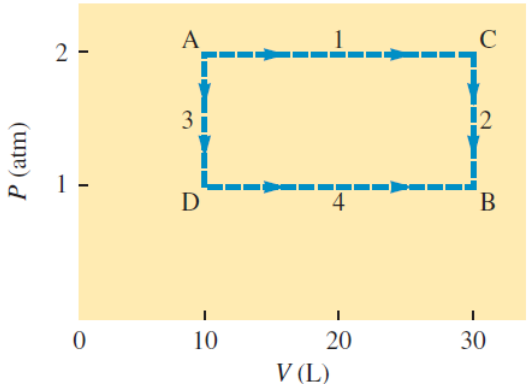


Summary

- Pathway one (steps 1 and 2):

$$q_{one} = q_1 + q_2 = 1.01 \times 10^4\ \text{J} - 4.56 \times 10^3\ \text{J}$$
$$= 5.5 \times 10^3\ \text{J}$$
$$w_{one} = w_1 + w_2 = -4.05 \times 10^3\ \text{J}$$
$$q_{one} + w_{one} = 1.5 \times 10^3\ \text{J} = \Delta E_{one}$$
$$\Delta H_{one} = \Delta H_1 + \Delta H_2$$
$$= 1.01 \times 10^4\ \text{J} - 7.60 \times 10^3\ \text{J}$$
$$= 2.5 \times 10^3\ \text{J}$$

Energy, Enthalpy, Heat, and Work Under Different Conditions

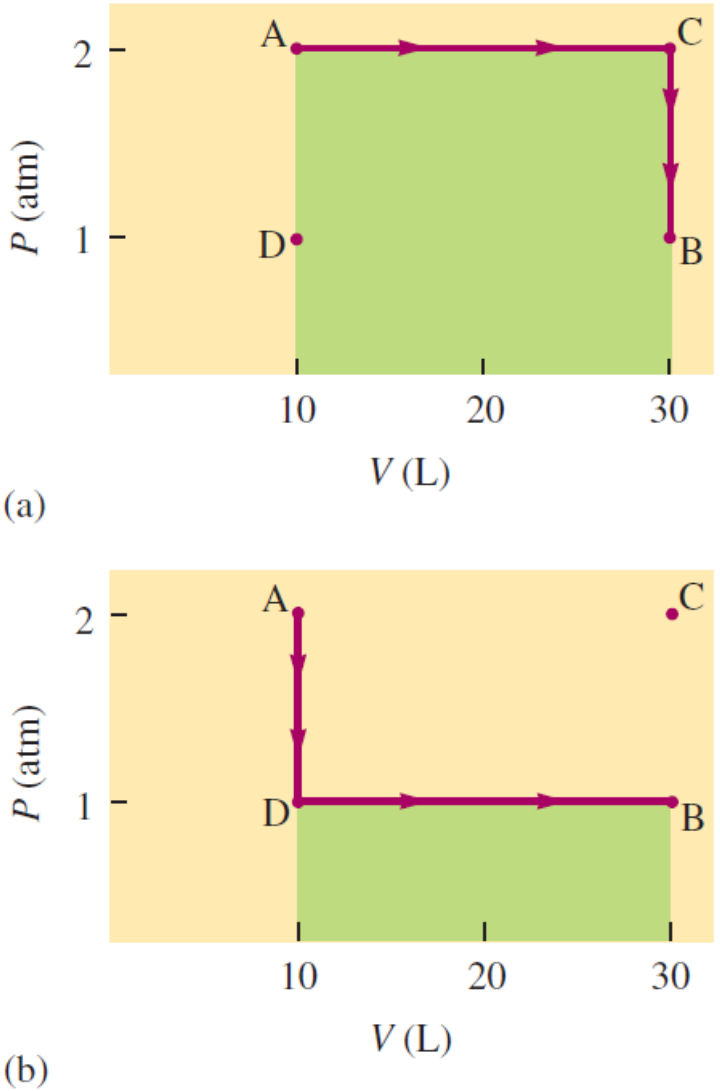


- Pathway two (steps 3 and 4):

$$q_{two} = q_3 + q_4 = -1.52 \times 10^3\ \text{J} + 5.08 \times 10^3\ \text{J}$$
$$= 3.56 \times 10^3\ \text{J}$$
$$w_{two} = w_3 + w_4 = -2.03 \times 10^3\ \text{J}$$
$$q_{two} + w_{two} = 3.55 \times 10^3\ \text{J} - 2.03 \times 10^3\ \text{J}$$
$$= 1.52 \times 10^3\ \text{J} = \Delta E_{two}$$
$$\Delta H_{two} = \Delta H_3 + \Delta H_4$$
$$= -2.53 \times 10^3\ \text{J} + 5.08 \times 10^3\ \text{J}$$
$$= 2.55 \times 10^3\ \text{J}$$

Energy, Enthalpy, Heat, and Work Under Different Conditions

The magnitude of the work for pathway one (a) and pathway two (b) is shown by the colored areas:
$| w | = | P\Delta V |$.



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
Ω

Macroscopic

Entropy
S

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

S is an extensive state function like E and H

For a combined system A+B

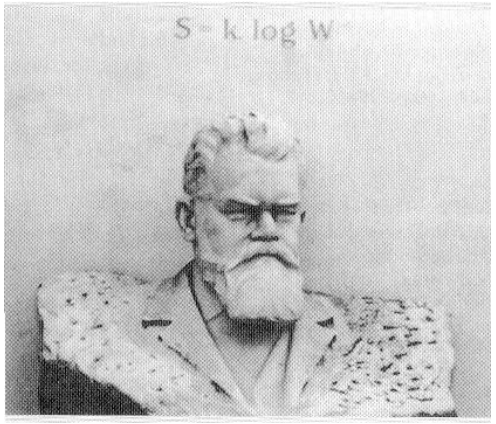
$$\Omega_{A+B} = \Omega_A \times \Omega_B \qquad S_{A+B} = S_A + S_B$$

$$S \propto \ln \Omega \Rightarrow \boxed{S = k_B \ln \Omega}$$

Entropy: Definition of Disorder in Thermodynamics

$$S = k_B \ln \Omega$$

State function



Ω = Number of ways corresponding to a given state

k_B = Boltzmann's constant = R/N_A

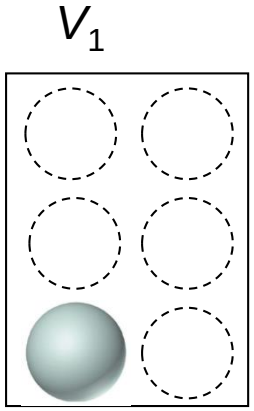
ΔS of a single ideal gas molecule

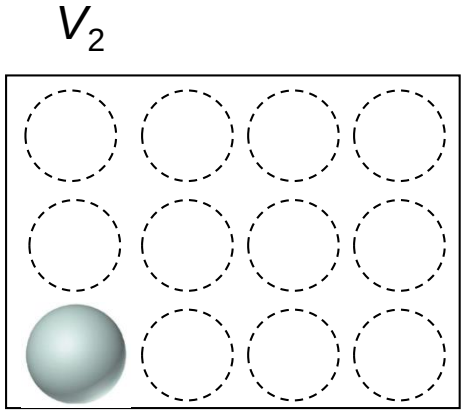
$$S = k_{\mathrm{B}} \ln \Omega$$

$$V_1 \rightarrow V_2$$

$$\Delta S = k_{\mathrm{B}} \left\{ \ln \Omega_2 - \ln \Omega_1 \right\}$$

$$\Delta S = k_{\mathrm{B}} \ln \frac{\Omega_2}{\Omega_1}$$

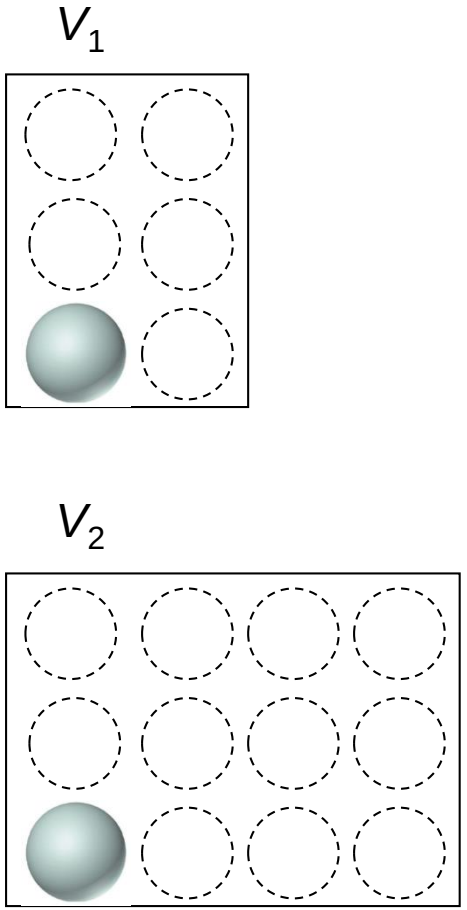




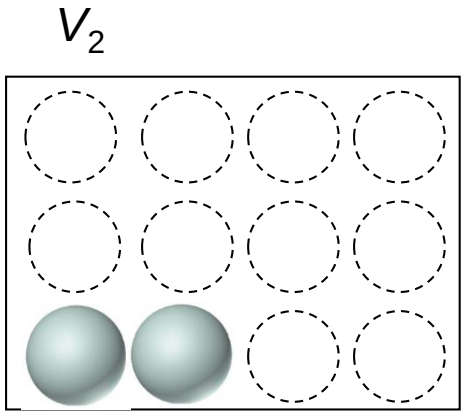
ΔS of a single ideal gas molecule

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

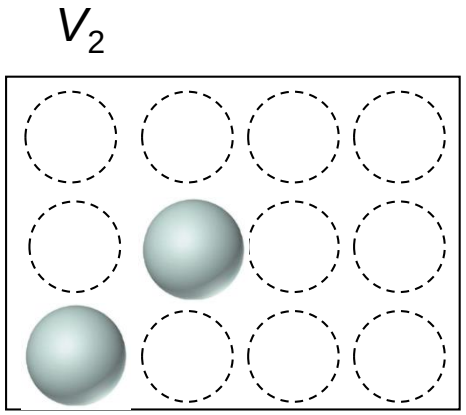
$$\Delta S = k_B \ln \frac{V_2}{V_1}$$



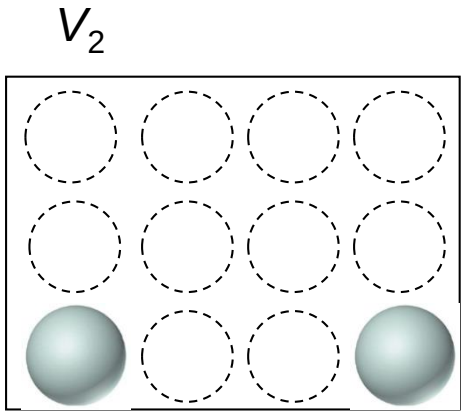
ΔS of two ideal gas molecules



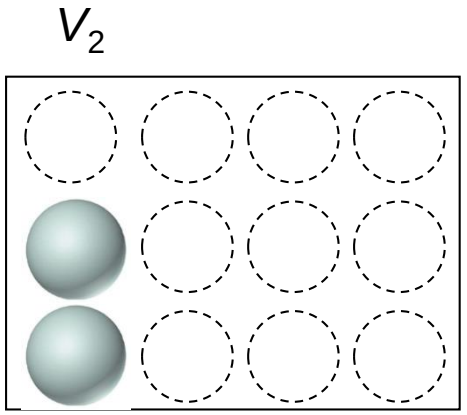
ΔS of two ideal gas molecules



ΔS of two ideal gas molecules

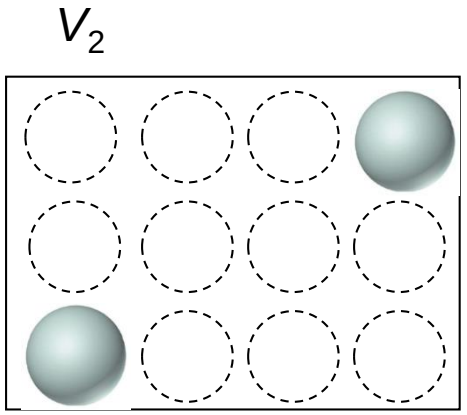


ΔS of two ideal gas molecules

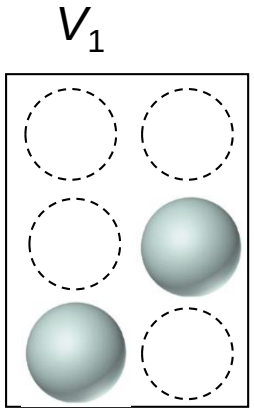


ΔS of two ideal gas molecules

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

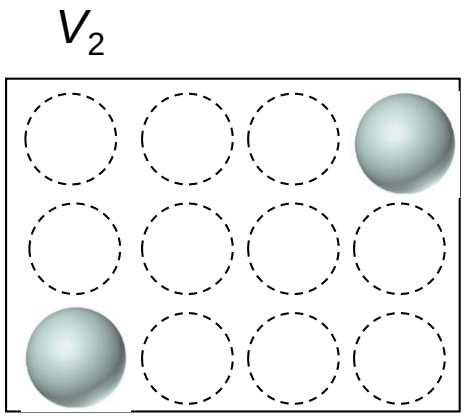


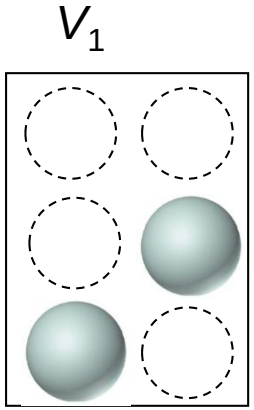
$$\Omega_1 \Rightarrow V_1 \times V_1$$



ΔS of two ideal gas molecules

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





ΔS of n moles of ideal gas molecules

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

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

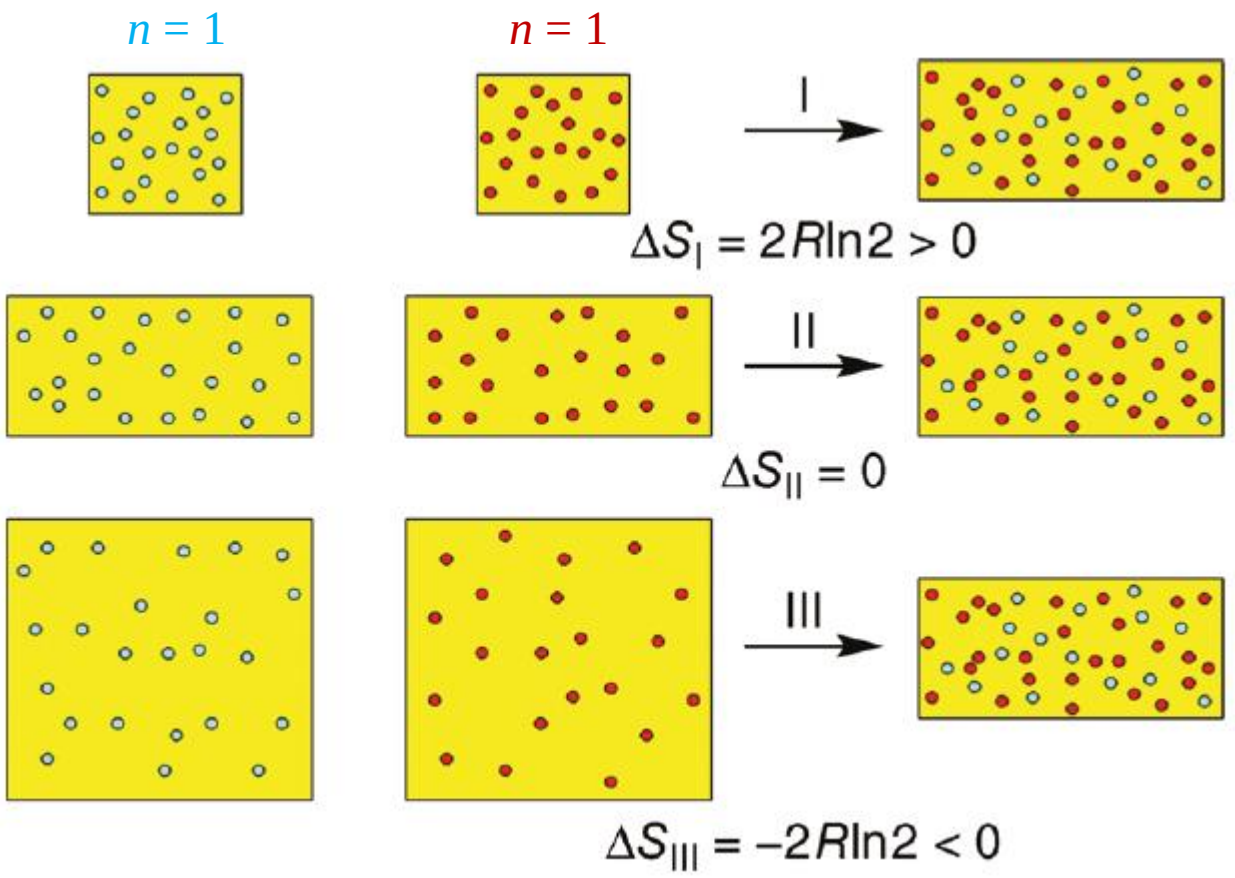
$$\Delta S = nN_A k_B \ln \frac{V_2}{V_1}$$

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

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

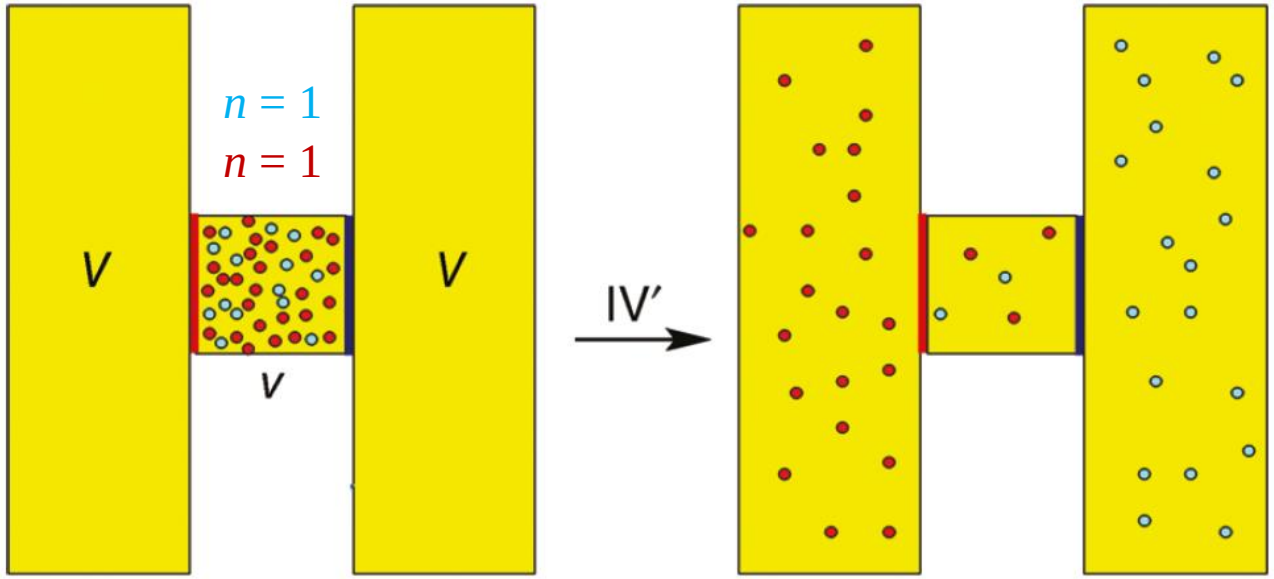
Mixing May Not Lead to Larger Entropy

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



Demixing May Not Lead to Smaller Entropy

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



$$\Delta S_{IV'} = 2R \ln\left(\frac{V}{v}\right) > 0$$

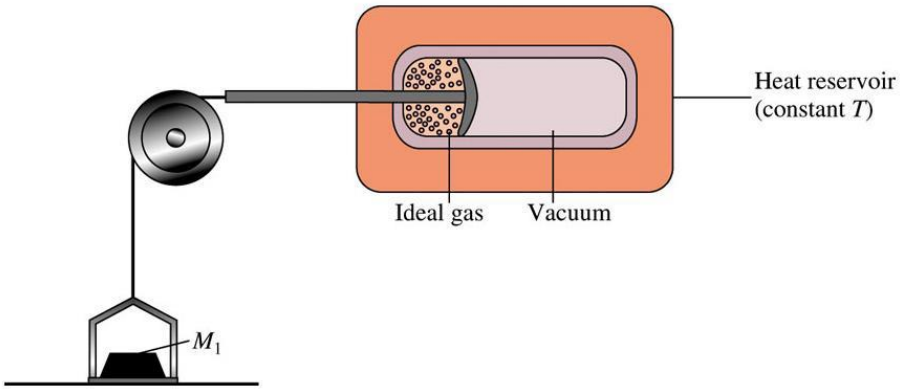
Heat Change of a Reversible Isothermal Process

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

$$w = -\int_{V}^{V'} P_{\text{ext}}\, dV \qquad P_{\text{ext}} \approx P = \frac{nRT}{V}$$

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 ΔS 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

ΔS_{sys}	ΔS_{surr}	ΔS_{univ}	
+	+	+	Spontaneous
–	–	–	Non-spontaneous
+	–	?	Depends on the relative size
–	+	?	

Total Entropy Change for Reversible Processes

Under equilibrium conditions:

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

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

Surrounding's point of view

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

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*:

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

ΔS_{surr} is primarily determined by the heat flow to or from the system.

$q < 0$: system → surrounding ⇨ S_{surr} increases
$q > 0$: system ← surrounding ⇨ S_{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 ΔS 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 → larger ΔS

High T → smaller ΔS

Heat flow: Low T → 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.

ΔS (melting, 273 K) = 22.00 J K^{-1} mol^{-1}

ΔH (melting, 273 K) = 6.006 kJ mol^{-1}

H_2O (ice, 283 K) $\rightarrow$ H_2O (liquid, 283 K)

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} = \Delta S_{\text{system}} - \frac{\Delta H}{T_{\text{surr}}}$$

$$= 22.00 - 6006 / 283 = 0.78 \text{ JK}^{-1} \text{ mol}^{-1}$$

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

Second Law of Thermodynamics

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

Under constant pressure and temperature ($q_{sys} = \Delta H$, $T = T_{surr}$):

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} - \frac{\Delta H}{T} \geq 0 \quad \Rightarrow \quad \Delta H - T\Delta S_{\text{system}} \leq 0$$

Define a new state function G for the system (Gibbs free energy):

$$G = H - TS$$ (In system's point of view)

Constant P and T

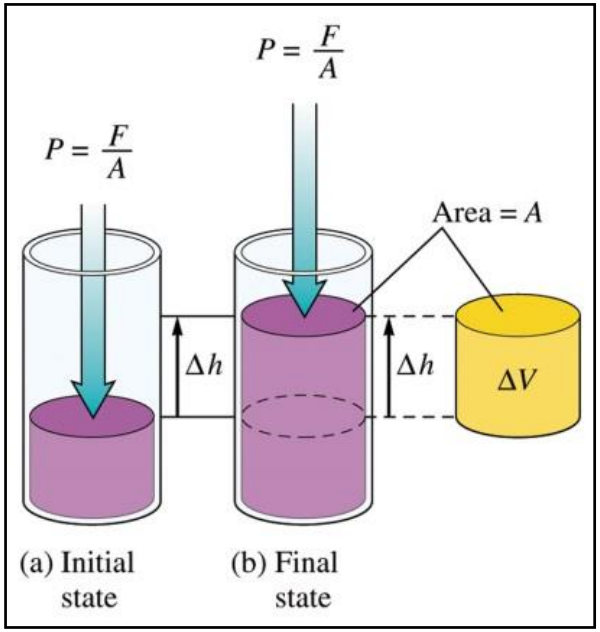
$$\Delta S_{universe} \geq 0 \quad \Rightarrow \quad \boxed{\Delta G = \Delta H - T\Delta S \leq 0}$$

Gibbs Free Energy and Work

$$w = w_{useful} + w_{PV}$$

$$w_{PV} = -P_{\text{ext}}\Delta V$$

- Lifting a weight
- Stretching a spring
- Electrical work (charging a battery)
- Transfer of particles



Gibbs Free Energy and Work

$$w = w_{useful} + w_{PV}$$

Constant *P* and *T*

$$\Delta E = q_P + w_{useful} - P\Delta V \qquad \text{(First law)}$$

$$\Delta H = \underbrace{q_P + w_{useful} - P\Delta V}_{\Delta E} + P\Delta V = q_P + w_{useful}$$

$$\Delta G = \Delta H - T\Delta S = q_P + w_{useful} - T\Delta S$$

Gibbs Free Energy and Work

$$\Delta G = \Delta H - T\Delta S = q_P + w_{useful} - T\Delta S$$

Reversible pathway

$$w_{useful} = w_{useful}^{\max} \qquad q_P = q_P^{rev}$$

$$\Rightarrow \quad \Delta G = q_P^{rev} + w_{useful}^{\max} - T\Delta S$$

$$\because \Delta S = \frac{q_P^{rev}}{T} \quad \Rightarrow \quad \Delta G = w_{useful}^{\max}$$

FREE to do work!

Second Law of Thermodynamics

$$\Delta G = \Delta H - T\Delta S \leq 0$$

ΔH	ΔS	ΔG	
+	+	?	Spontaneous at high *T* Non-spontaneous at low *T*
–	–	?	Non-spontaneous at high *T* Spontaneous at low *T*
+	–	+	Non-spontaneous
–	+	–	Spontaneous

In general: ΔS is more important at higher T!

Learning Check

Predict the entropy change of the system for the following reactions:

	ΔS
$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$	–
$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$	+
$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$	+

Gibbs Free Energy at Different *T* and *P*

$$dE = dq + dw$$

$$= TdS - PdV$$

Combined 1st and 2nd laws

$$\Delta E = q + w$$

$$dS = dq/T$$

$$dw = -PdV$$

$$dH = dE + PdV + VdP$$

$$= TdS - PdV + PdV + VdP$$

$$= TdS + VdP$$

$$H = E + PV$$

Gibbs Free Energy at Different *T* and *P*

$$dH = TdS + VdP$$

$$dG = dH - TdS - SdT \qquad G = H - TS$$

$$= TdS + VdP - TdS - SdT$$

$$= VdP - SdT$$

V and *S* are parameters
P and *T* are variables

$$G \rightarrow G(P,T)$$

Gibbs Free Energy at Different *T* and *P*

$$dG = VdP - SdT$$

$$G \rightarrow G\left(P,T\right)$$

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

Const. *T*

$$\int_{G^0}^{G} dG = \int_{P^0}^{P} VdP$$

Gibbs Free Energy at Different *T* and *P*

$$\int_{G^0}^{G} dG = \int_{P^0}^{P} V dP$$

For the ideal gas we set

$V = nRT / P$

$$\int_{G^0}^{G} dG = nRT \int_{P^0}^{P} \frac{dP}{P}$$

$$G - G^0 = nRT \ln \frac{P}{P^0}$$

Standard states

Gibbs Free Energy at Different *T* and *P*

$$G - G^0 = nRT \ln \frac{P}{P^0} = nRT \ln a$$

By convention we set P^0 = 1 atm and we replace P by activity (effective pressure).

$$\mu = \mu^0 + RT \ln a$$

where μ is the Gibbs free energy for one mole of substance, or the chemical potential.

Chemical Potential

State A

State B

$\Delta G < 0$, second law

$$\mu = \mu^0 + RT \ln a$$

where μ is the Gibbs free energy for one mole of substance, or the chemical potential.

Gibbs Free Energy and Reaction Quotient

$$G = G^0 + nRT \ln a$$

$$\mathrm{A} + \mathrm{B} \rightarrow 2\mathrm{C}$$

$$\Delta G = \sum G \ (\text{products}) - \sum G \ (\text{reactants})$$

$$= \Delta G^0 + RT\left(2\ln a_C - \ln a_A - \ln a_B\right)$$

$$\Delta G^0 = 2G_C^0 - G_A^0 - G_B^0$$

$$\Delta G = \Delta G^0 + RT \ln Q \qquad Q = \frac{a_C^2}{a_A a_B}$$

ΔG and Reaction Quotient

$$\Delta G = \Delta G^0 + RT \ln Q$$

$$\mathrm{A} + \mathrm{B} \rightarrow 2\mathrm{C}$$

$$\Delta G^0 = 2G_C^0 - G_A^0 - G_B^0$$

$$\Delta G^0 = 2\Delta G_f^0(\mathrm{C}) - \Delta G_f^0(\mathrm{A}) - \Delta G_f^0(\mathrm{B})$$

Standard Gibbs energy of formation

Learning Check

$$\Delta G = \Delta G^0 + RT \ln Q$$

E.g. $CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$

Calculate ΔG with P_{CO} = 5.0 atm and P_{H_2} = 3.0 atm at 25 °C

ΔG_f^o (CH_3OH) = –166 kJ/mol

ΔG_f^o (CO) = –137 kJ/mol

ΔG° = (–166) – (–137) – 2(0) = –29 kJ

$$\Delta G = -2.9 \times 10^4 + (8.314)(298) \ln \frac{1}{5 \times 3^2}$$

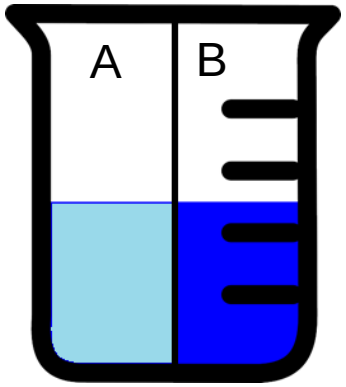
$= -3.8 \times 10^4$ J per mol of CO

Spontaneously generate more CH_3OH

Learning Check

Calculate the change in Gibbs free energy for the diffusion of sugar molecules through the membrane at room temperature.

[Sugar] = 10. mM



[Sugar] = 150. mM

$$G_A = G_A^0 + nRT \ln 10 \qquad G_B = G_B^0 + nRT \ln 150$$

$$\text{Sugar}\left(150\ \text{mM}\right) \rightarrow \text{Sugar}\left(10\ \text{mM}\right)$$

$$\Delta G = G_A - G_B = RT \ln \frac{10.}{150.} = -6.7\ \text{kJ mol}^{-1} < 0$$

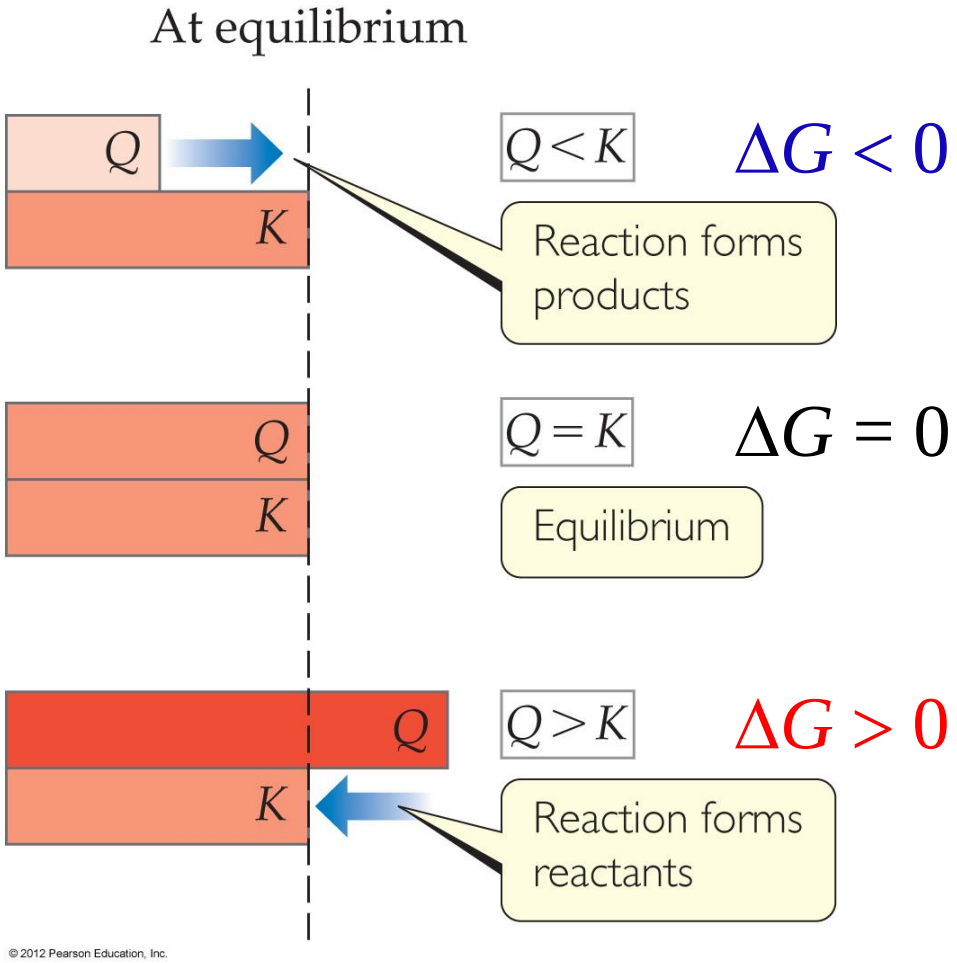
ΔG^0 and Equilibrium Constants

$$\Delta G = \Delta G^0 + RT \ln Q$$

Equilibrium ($\Delta G = 0$) $\Rightarrow$ $\boxed{\Delta G^0 = -RT \ln K_{eq}}$

$$\Delta G = -RT \ln K_{eq} + RT \ln Q = RT \ln \frac{Q}{K_{eq}}$$

ΔG and Reaction Direction

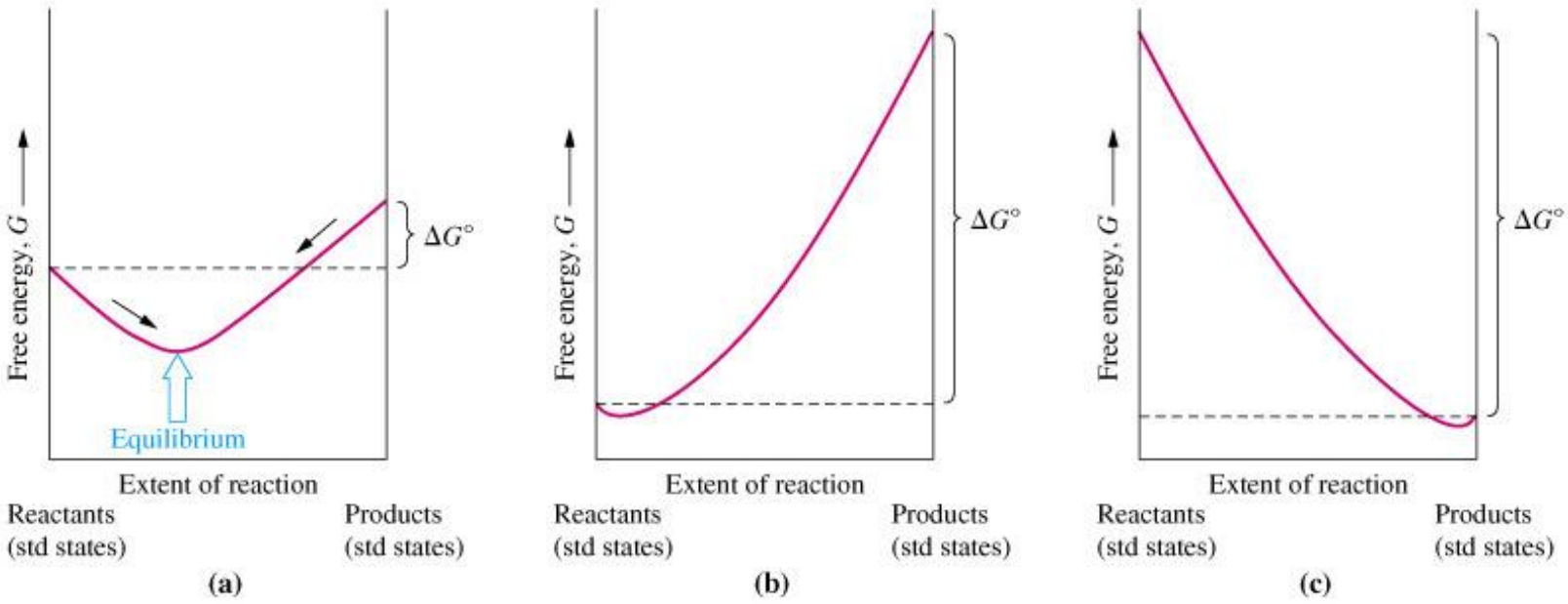


$$\Delta G = RT \ln \frac{Q}{K_{eq}}$$

ΔG and Reaction Direction

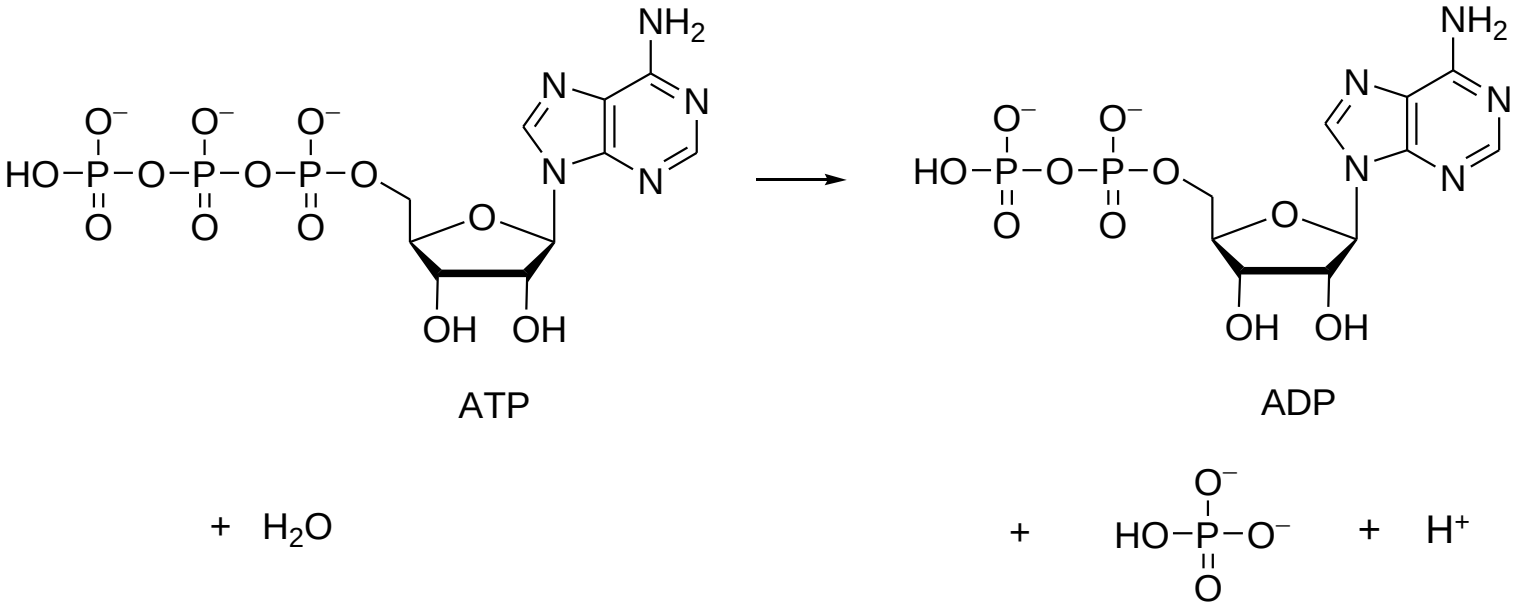
$$\Delta G = \Delta G^0 + RT \ln Q$$

$$\Delta G^0 = -RT \ln K_{eq}$$



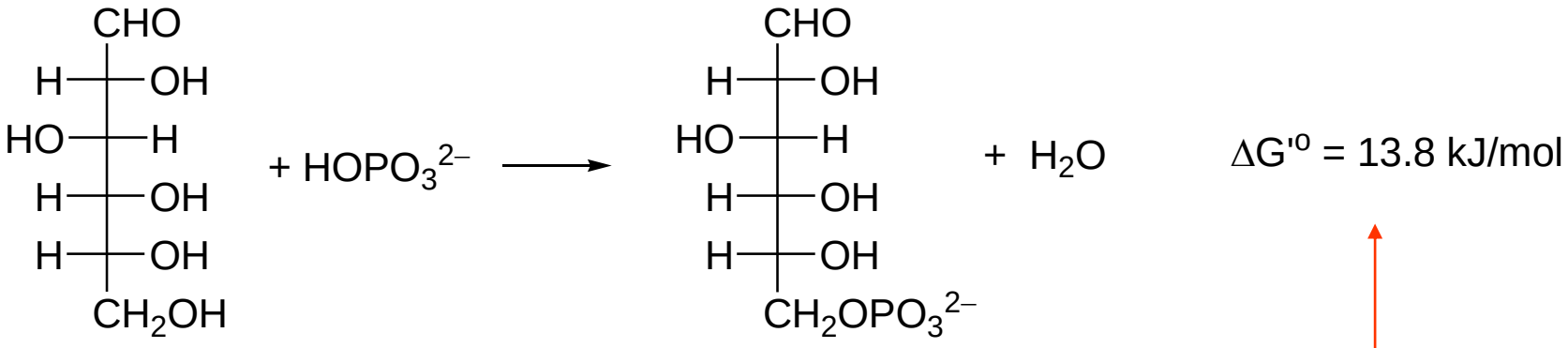
※ Biological relevance

$ATP + H_2O \rightarrow ADP + HPO_4^{2-} + H^+$ $\quad \Delta G'^0 = -30.5$ kJ/mol



$\Delta G'^0$: at pH 7 and certain salt concentrations

E.g.



Solution of our body:

$$\text{Glucose} + HOPO_3^{2-} \longrightarrow \text{Glucose 6-phosphate} + H_2O \qquad \Delta G'^{o} = 13.8 \text{ kJ/mol}$$

$$ATP + H_2O \longrightarrow ADP + HOPO_3^{2-} + H^+ \qquad \Delta G'^{o} = -30.5 \text{ kJ/mol}$$

$$\text{Glucose} + ATP \longrightarrow \text{Glucose 6-phosphate} + ADP + H^+ \qquad \Delta G'^{o} = -16.7 \text{ kJ/mol}$$

With the help of ATP hydrolysis, the phosphorylation of glucose is now more favorable!

Final Remarks on the Second Law

Why life is mortal?

More than 30,000 compounds in our body are synthesized by non-spontaneous reactions and therefore they are all metastable

Why we are alive?

Activation energy, our guarding angel

Think: diamond will not change into graphite in front of your eyes…

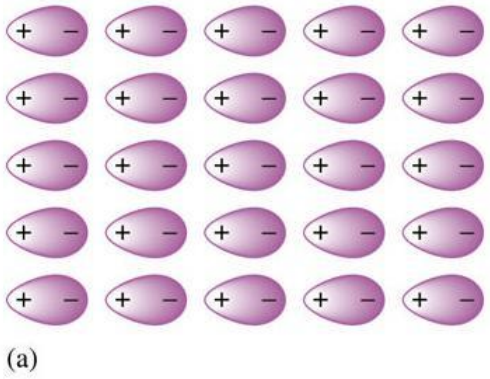
Third Law of Thermodynamics

The entropy of a perfect crystal at absolute zero is exactly equal to zero.

$$S = k_B \ln \Omega$$

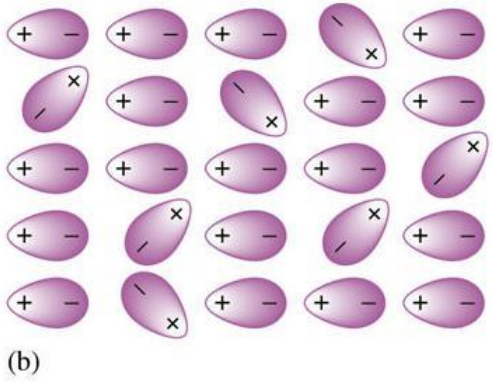
Walter Nernst

$S = 0$



$T = 0$ K

$S > 0$



$T > 0$ K; Lattice vibration

Absolute Entropies

$$dS = \frac{dq_{rev}}{T}$$

Heat capacity is closely related to the system entropy!

$$dS = \frac{nC\ dT}{T}$$

C is C_P or C_V

$$S(T) = \int_0^T \frac{nC\ dT}{T}$$

$S(0) = 0$

0 Kelvin?

Measurements can be and have been made down to 0.1 K and the heat capacity below measurable range can be accurately estimated.

Substance	S^0_{298} (J K^{-1}mol^{-1})
$H_2(g)$	131
HBr (g)	199
$H_3PO_4(aq)$	158
KCl (s)	83
$Al_2O_3(s)$	51

$$\Delta S^0_{reaction} = \sum S^0_{products} - \sum S^0_{reactants}$$

$$Al_2O_3(s) + 3H_2(g) \rightarrow 2Al\,(s) + 3H_2O\,(g)$$

Substance	$S^0_{298}(\text{J K}^{-1}\text{mol}^{-1})$
$H_2(g)$	131
$H_2O\,(g)$	189
$Al\,(s)$	28
$Al_2O_3(s)$	51

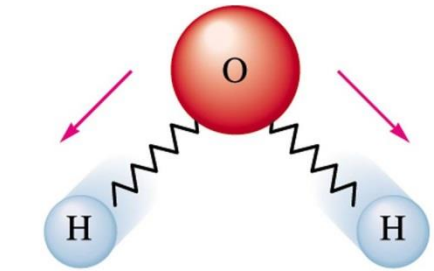
$$\Delta S^0_{reaction} = 2 \times 28 + 3 \times 189 - (3 \times 131 + 51)$$

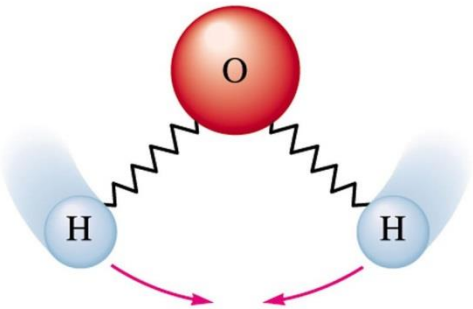
$$= 179\,\text{J/K}$$

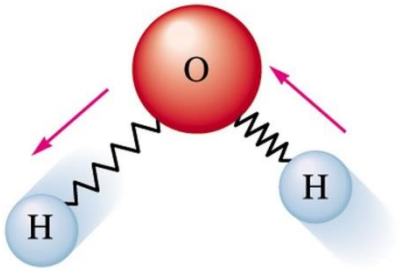
Why is there an increase in *S* ?

$$Al_2O_3(s) + 3H_2(g) \rightarrow 2Al\,(s) + 3H_2O\,(g)$$

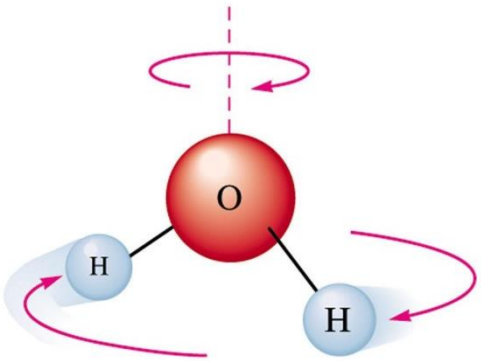
$$\Delta S^0_{reaction} = 179\,\mathrm{J/K}$$







Vibrations



Rotation