Thermodynamics

Thermodynamics vs. **Kinetics**

Kinetics is concerned with reaction rates

Thermodynamics is concerned with energy of reactants versus products

Thermodynamics is concerned with the position of equilibrium

In chemistry we are interested in whether a particular reaction

will “go”

usually means a favorable equilibrium and a conveniently rapid rate

Or will “not go”

either an unfavorable equilibrium or a rate too slow to be useful

Spontaneous Processes and Entropy

Spontaneous Processes

We describe a process as "spontaneous" or "nonspontaneous."

Product favored equilibrium: (spontaneous process)

Whether a reaction is spontaneous or not has nothing to do with its rate.

A spontaneous reaction can be very fast or can be so slow that it appears not to take place at all

Examples of spontaneous processes

A gas expands into a vacuum spontaneously, but does not flow out of its container to form a vacuum spontaneously.

Water freezes below 0°C spontaneously; ice melts above 0 °C spontaneously.

$$2Na(s) + 2H_2O(l) \longrightarrow H_2(g) + 2NaOH(aq)$$

spontaneous

$$H_2(g) + 2NaOH(aq) \longrightarrow 2Na(s) + 2H_2O(l)$$

nonspontaneous

We have emphasized enthalpy in our earlier discussions of thermodynamics

Our expectation is that a reaction that leads to a decrease in the total energy of the system should be spontaneous (ΔH is negative; reaction is exothermic).

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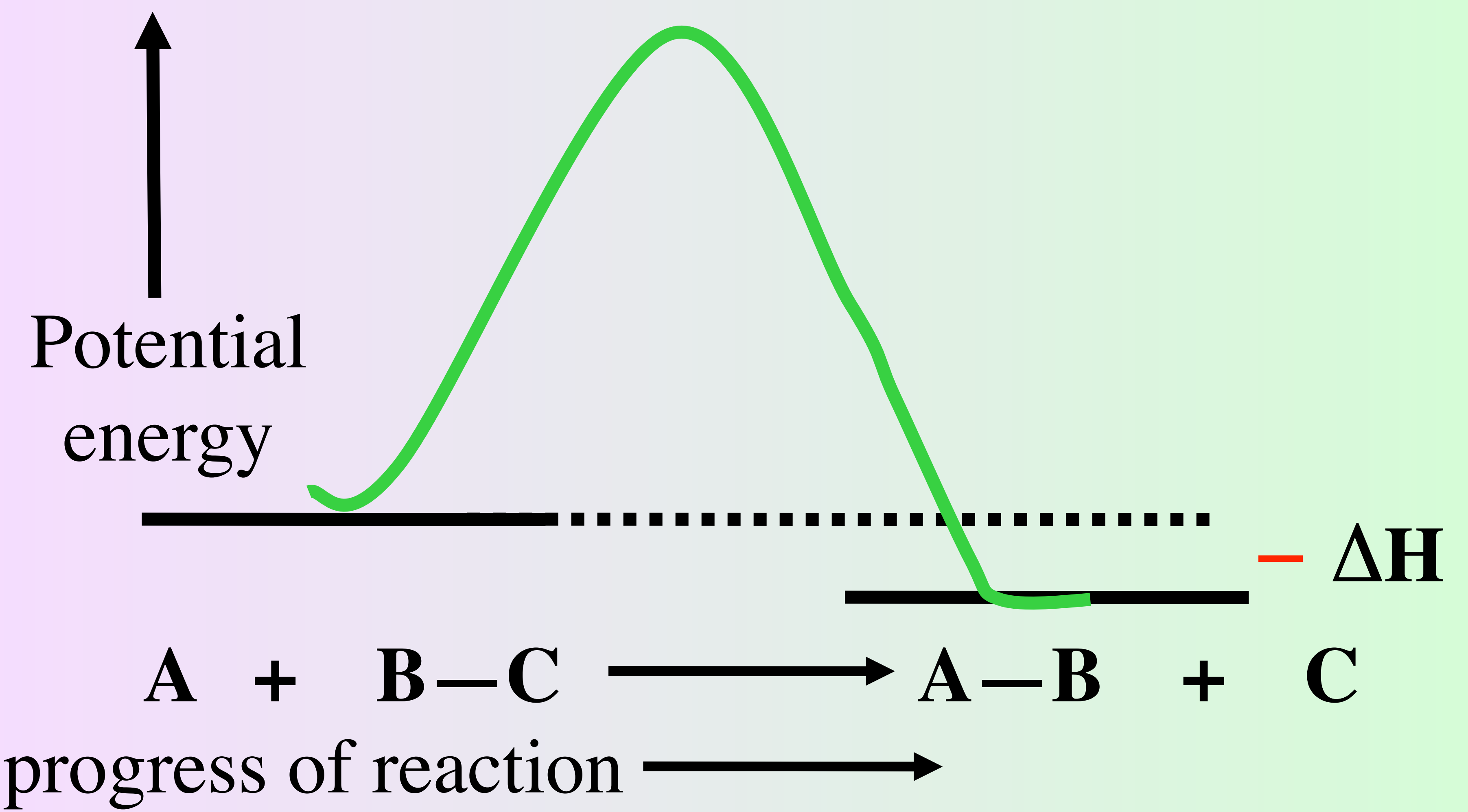

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Our expectation is that a reaction that leads to a decrease in the total energy of the system should be spontaneous (ΔH is negative; reaction is exothermic).

But observation tells us that enthalpy alone is an insufficient indicator of spontaneity.

some endothermic reactions are spontaneous

spontaneity depends on temperature; some reactions are spontaneous at one temperature, but nonspontaneous at another

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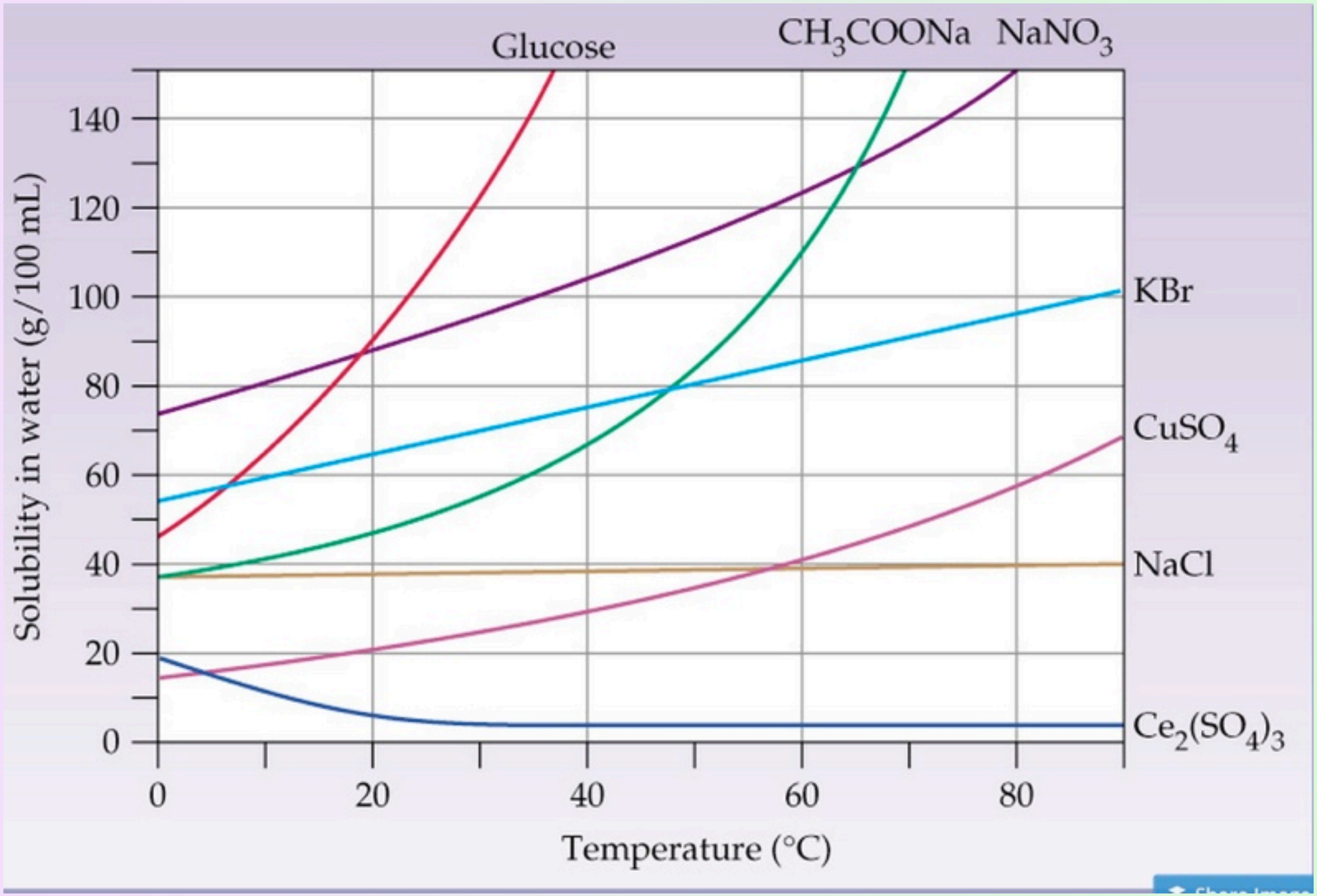


Two examples of spontaneous endothermic processes

ice melts spontaneously at temperatures above 0 ºC

$$\mathbf{H_2O(s) \longrightarrow H_2O(\mathit{l}) \quad \Delta \mathit{H}^{\circ} = +\,6.01\ kJ}$$

ammonium nitrate dissolves in water

$$\mathbf{NH_4NO_3(s) \longrightarrow NH_4^{+}(\mathit{aq}) + NO_3^{-}(\mathit{aq})}$$

$$\mathbf{\Delta \mathit{H}^{\circ} = +\,25\ kJ}$$

Four possibilities; examples of all four are known

exothermic – spontaneous

exothermic – nonspontaneous

endothermic –spontaneous

endothermic –nonspontaneous

Entropy

A process is spontaneous if it leads to an increase in the entropy of the universe.

Entropy is a measure of the randomness or disorder of a system.

Entropy is related to probability.

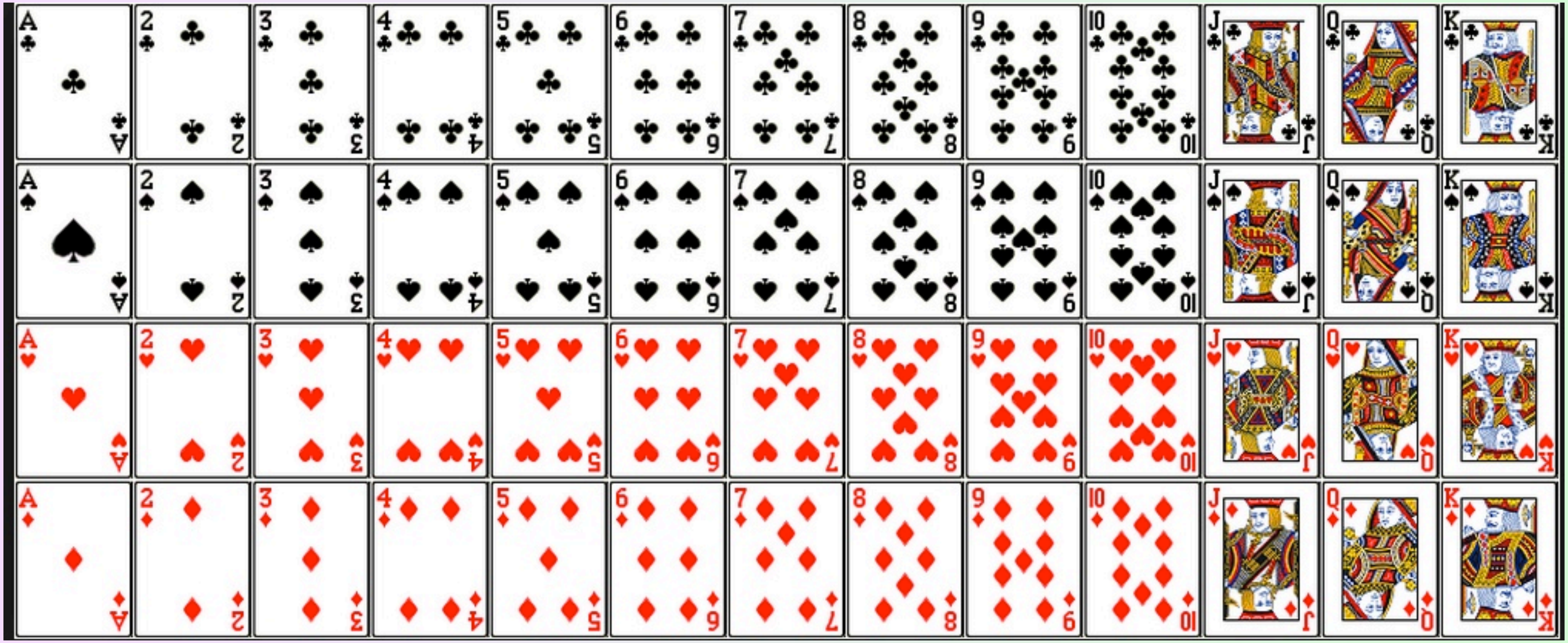
Probability

a probable event is one that can happen in many ways

an improbable event is one that can happen in only one way

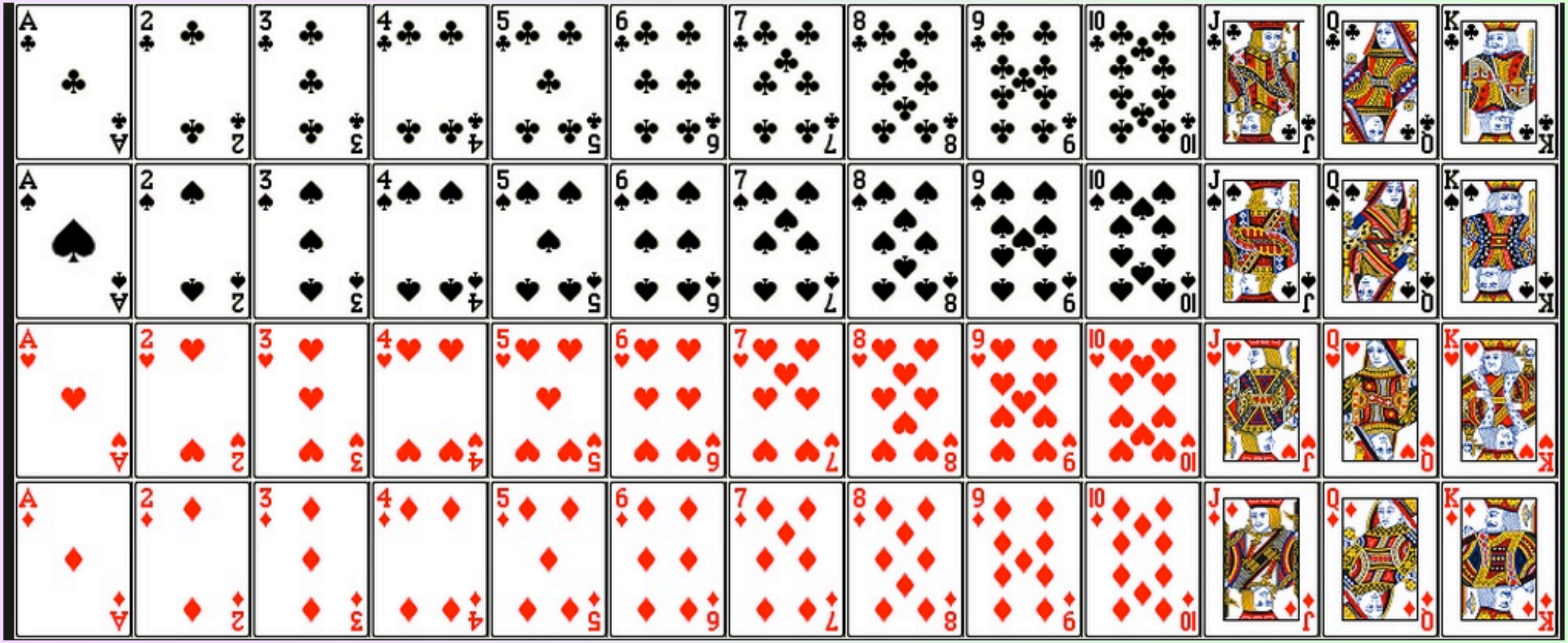
Probability

I throw a deck of cards in the air. What chance that they land arranged in this order?



Probability

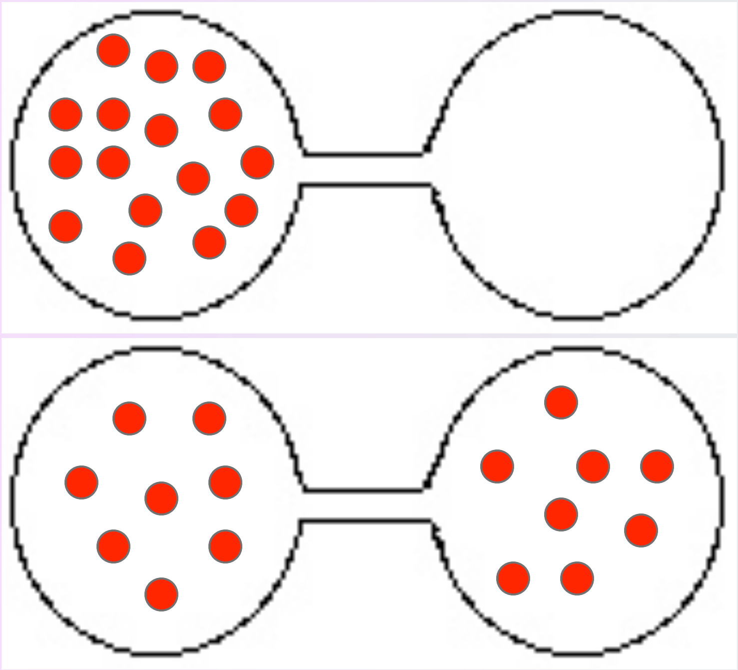
one in 8.07×10^{67}



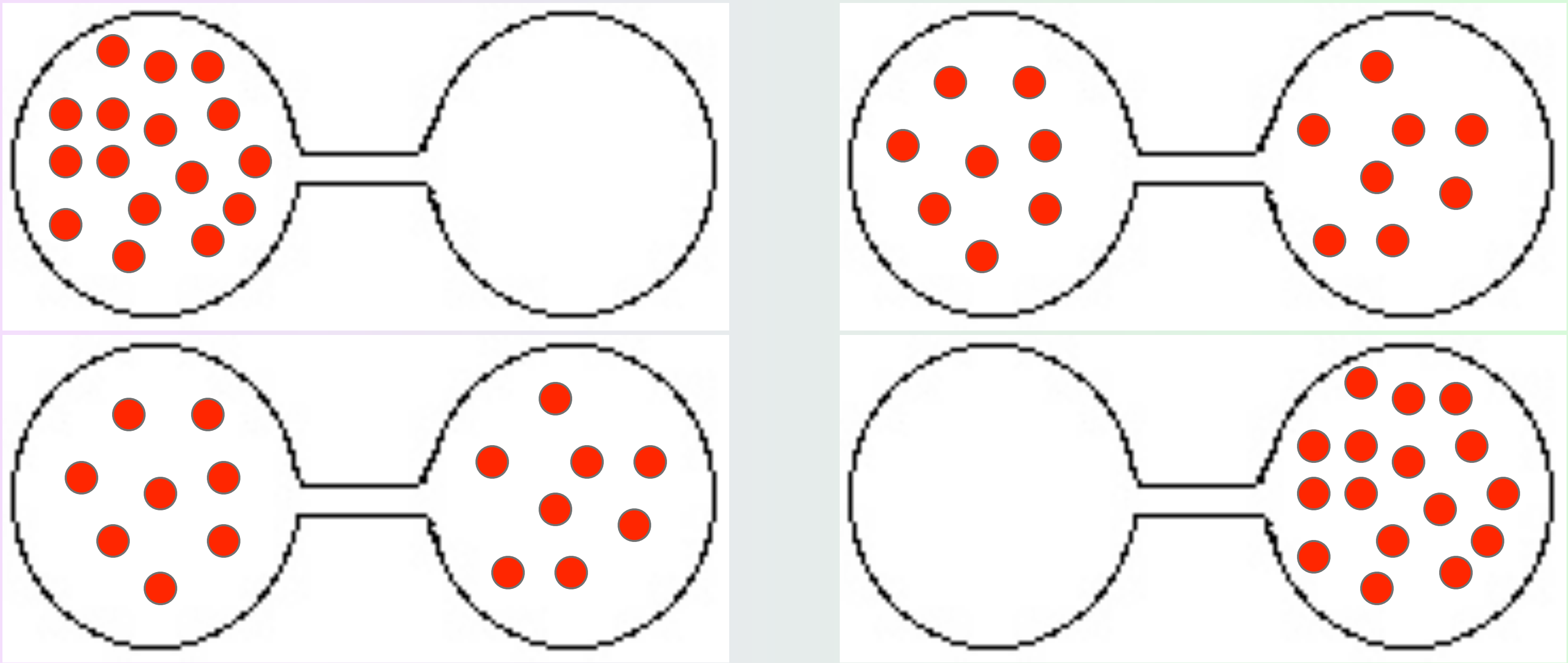
Entropy and Probability

Expansion of ideal gas into a vacuum is spontaneous, but migration of gas molecules into one region of a container is nonspontaneous.

expansion of ideal gas into a vacuum is spontaneous



expansion of ideal gas into a vacuum is spontaneous



but migration of gas molecules into one region of a container is nonspontaneous

Why is the spontaneous process the one that gives equal numbers of gas molecules in both flasks?

It is the most probable state -- the one that has the most ways of being achieved.

An ordered state has a low probability of occurring and a small entropy, while a disordered state has a high probability of occurring and a high entropy

For any substance, entropy increases

solid $\longrightarrow$ liquid $\longrightarrow$ gas

$$S_{solid} < S_{liquid} < S_{gas}$$

Entropy v.s Enthalpy

it is possible to determine absolute entropy (S) as opposed to enthalpy (H)

$S = J/K$ $\Delta H = kJ$

$S^o = J/Kmol$ $\Delta H^o = kJ/mol$

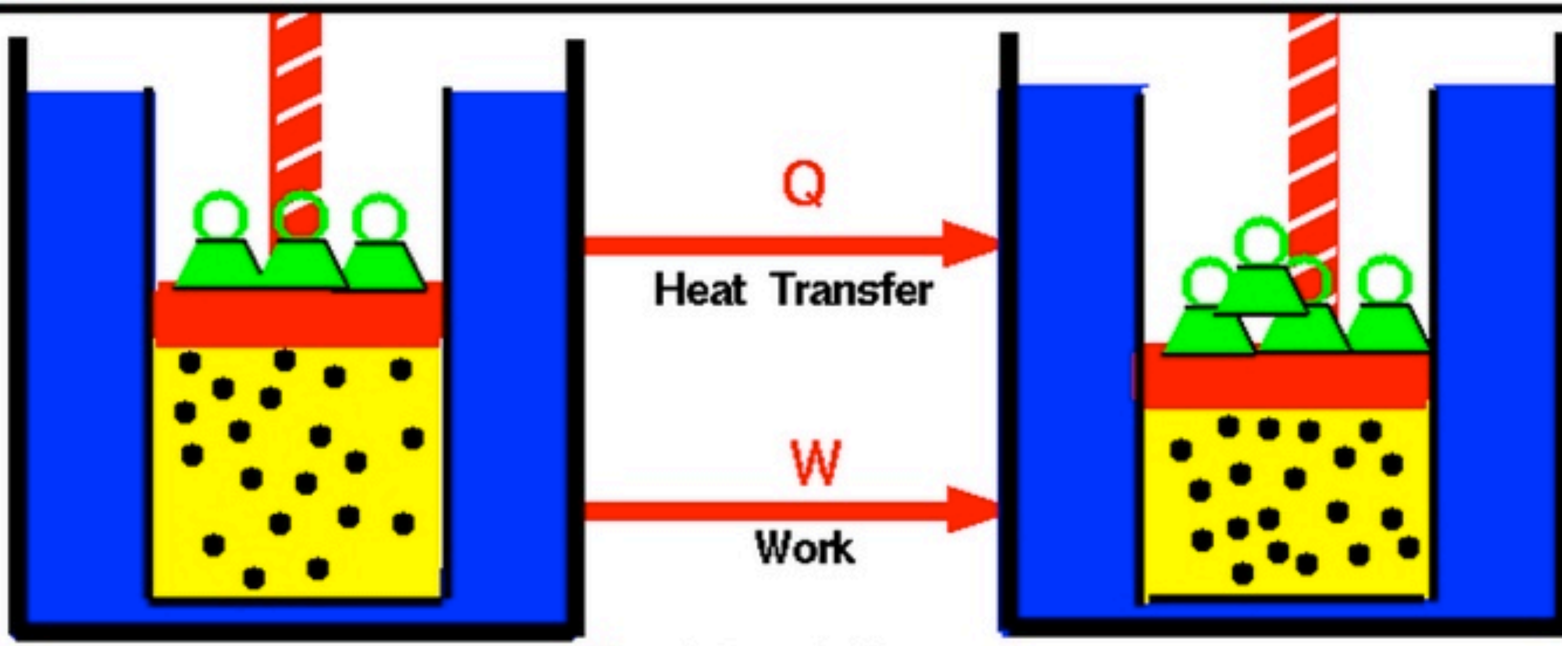
(for a mole of substance)

Some standard entropy values (S°)

substance	S° (J/K·mol)
$H_2O(l)$	69.9
$H_2O(g)$	188.7
$Br_2(l)$	152.3
$Br_2(g)$	245.3
$I_2(s)$	116.7
$I_2(g)$	260.7
C (diamond)	2.44
C (graphite)	5.69

First Law of Thermodynamics

Glenn Research Center



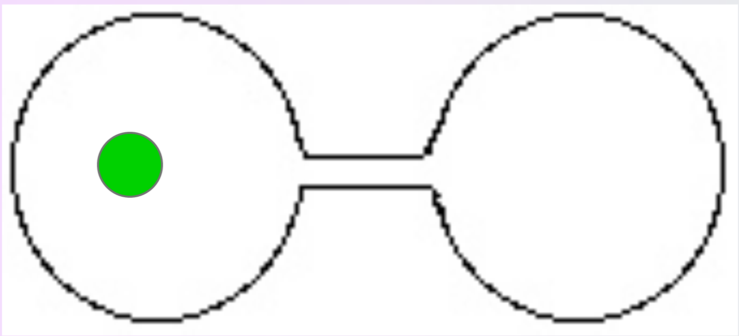
State 1 State 2

E = Internal Energy

$$E_2 - E_1 = Q - W$$

Any thermodynamic system in an equilibrium state possesses a state variable called the internal energy (E). Between any two equilibrium states, the change in internal energy is equal to the difference of the heat transfer into the system and work done by the system.

How many ways may 1 gas molecule be arranged in a two-bulb container?



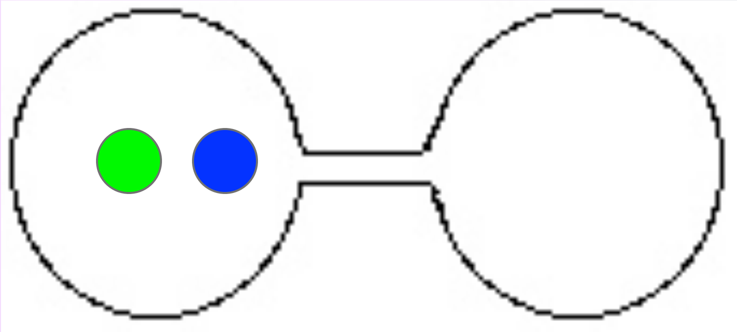
Left	Right
1	0
0	1

probability that the gas molecule will be in left bulb = .5

$$\boxed{\frac{1}{2^n}}$$

where n = number of molecules

What is the probability that two gas molecules will be in the same bulb of a two-bulb container?



Left	Right
both	0
green	blue
blue	green
0	both

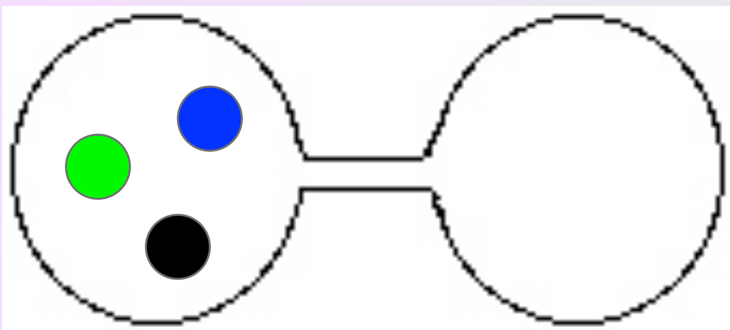
probability that both gas molecules will be in left bulb =

0.25

$$\frac{1}{2^n} = \frac{1}{2^2}$$

where n = number of molecules

What is the probability that 3 gas molecules will be in the same bulb of a two-bulb container?



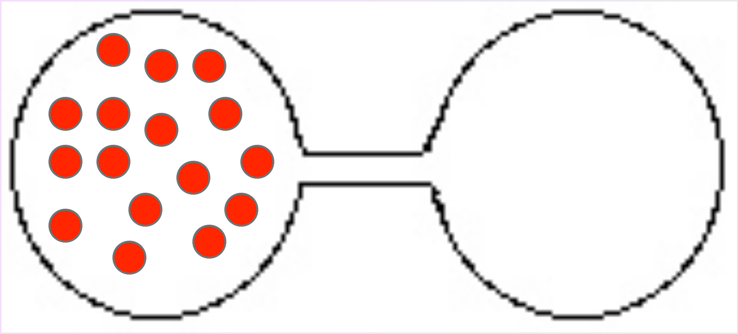
Left	Right	
3	0	
2	1	3 ways
1	2	3 ways
0	3	

probability that all gas molecules will be in left bulb = .125

$$\frac{1}{2^n} = \frac{1}{2^3}$$

where n = number of molecules

What is the probability that one mole of gas molecules will be in the same bulb of a two-bulb container?

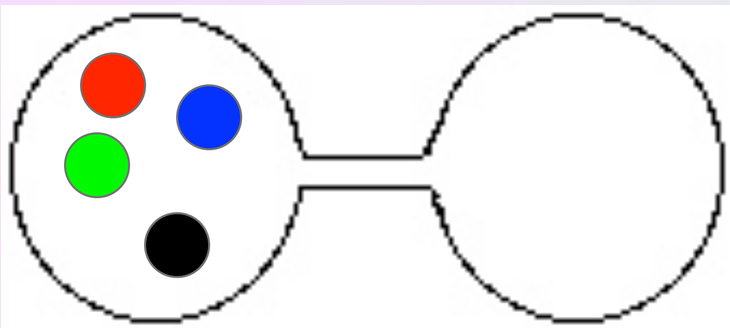


probability that all gas molecules will be in left bulb is very small

$$\frac{1}{2^n} = \frac{1}{2^N}$$

where n = Avogadro's number of molecules

What is the probability that 4 gas molecules will be equally distributed in a two-bulb container?



Left	Right	No. of ways
4	0	1 ways
3	1	4ways
2	2	6 ways
1	3	4ways
0	4	1 ways

16 possibilities

$$\frac{6}{16}$$

Equal distribution is the most probable out come