MME 2009 Metallurgical Thermodynamics

Entropy

So far changes in the state of systems that occur within the restrictions of the first law of thermodynamics were considered:

Energy is transferred from one state to another by any possible forms, unchanged in total quantity

Heat and work are the means of energy transfer and internal energy is the main stored energy that we focused on

Everyday practice dictates that some of the energy is wasted during transfer

Waste is a relative definition since one man's garbage is another's treasure

Energy dispersion rather than waste describes the result of ordinary processes in daily life

Electrical energy is free to disperse into wire and then to air rather than water in the kettle
Chemical energy is free to disperse into the engine and then to the car instead of applying torque to the crankshaft
Wind energy is free to push the clouds instead of pushing wind turbines

Energy is dispersed in all spontaneous, natural processes to other possible forms as predicted by the first law of thermodynamics

Complete conversion of one form of energy to another, or reversible processes never occur in nature

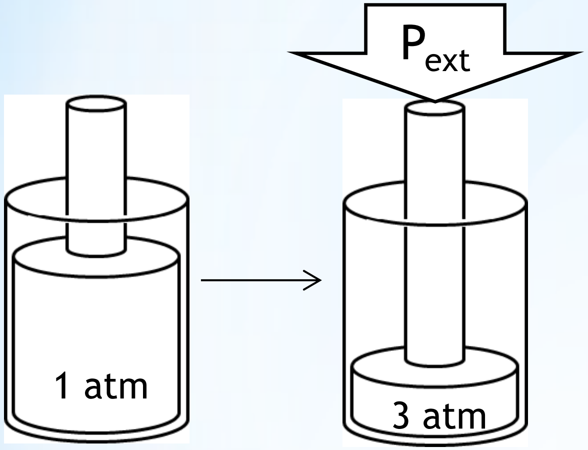
It is an engineer's goal to completely convert energy to the desired form with the maximum efficiency

Hence reversible process is a man-made concept and impossible to occur in the nature within an observable period of time

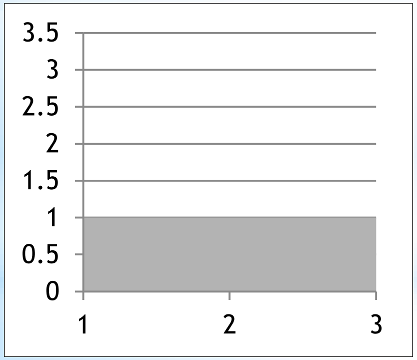
It is possible for a process to occur reversibly if enough time and care is provided to keep the path of the process moving through infinitely many equilibrium states

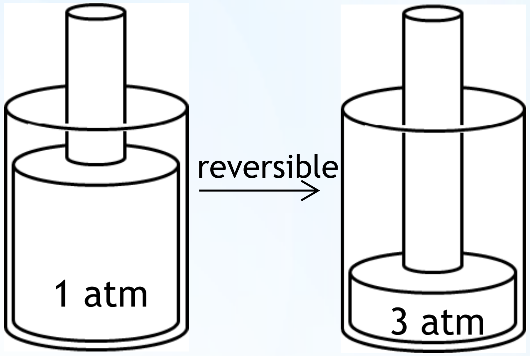
Unfortunately, the achievements of the human civilization so far have been far from maximum efficiency, reversibility and sustainability. Although invention of fire, steam engine, electricity have gradually improved the efficiency with which man used energy to satisfy his growing needs, Earth suffered irreversible damage as a result of careless engineering

Reversible processes are considered in thermodynamic calculations to estimate the maximum work output

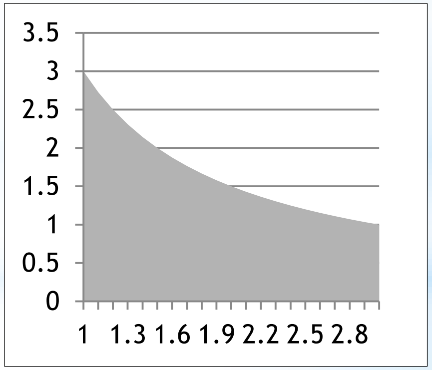


$$P_{ext} >> P, \qquad \Delta W = P\Delta V$$





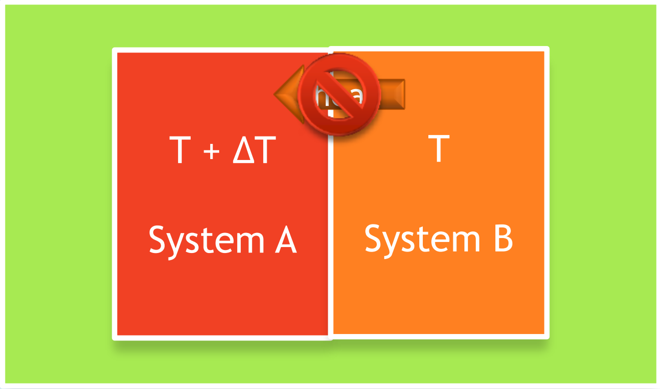
$$P_{ext} \approx P, \quad W = \int_{V1}^{V2} PdV$$



Although it is hard to conduct a reversible process, calculating the property changes through reversible processes is easy since intensive and extensive properties of matter are experimentally measured at equilibrium conditions

Zeroth law of thermodynamics describes the spontaneous heat flow direction between two bodies as always from hot to cold

Consider two systems in thermal contact isolated from the surroundings



T + ΔT

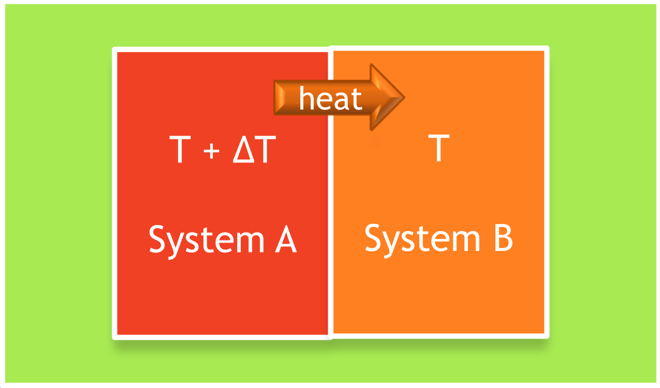
System A

T

System B

Energy never disperses toward thermal unequilibrium

Although it does not contradict with the first law:
Energy is conserved



heat

T + ΔT

System A

T

System B

Energy dispersion towards lower thermal equilibrium

$Q_A < 0$, $Q_B > 0$, same magnitude of heat transferred

$Q_A + Q_B = 0$

$$\left|\frac{Q_A}{T_A}\right| < \left|\frac{Q_B}{T_B}\right|$$

$$\frac{Q_A}{T_A} + \frac{Q_B}{T_B} > 0 \; for\ all\ systems\ in\ thermal\ contact$$

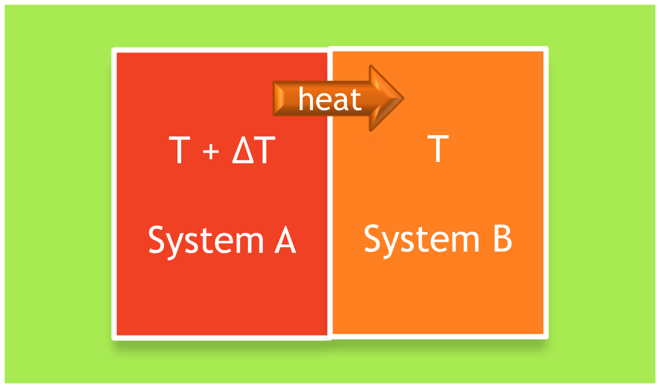
Q = H for systems under constant pressure

$$\frac{\Delta H_{system}}{T_{system}} = \Delta S, new\ state\ property: entropy$$

Entropy is a measure of how dispersed the energy of a system is among the different possible ways that system can contain energy

Entropy must increase for irreversible processes

Spontaneous heat flow between two isolated systems in thermal contact is irreversible

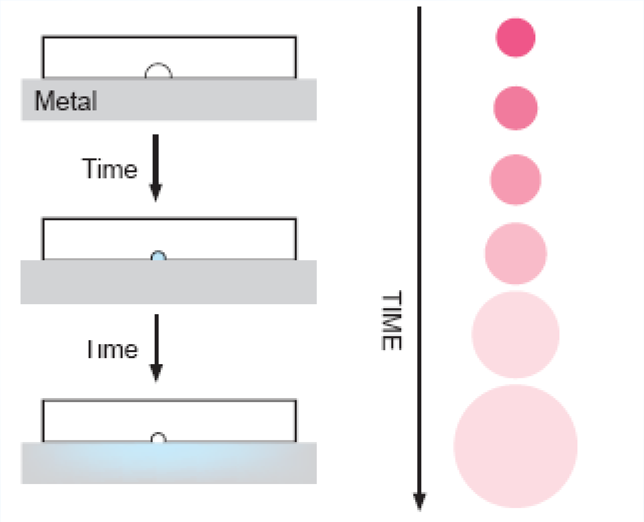


$$\Delta S = \Delta S_A + \Delta S_B > 0$$

Example – Evaporation of alcohol from a metal surface

Alcohol requires heat to evaporate since it is an endothermic reaction

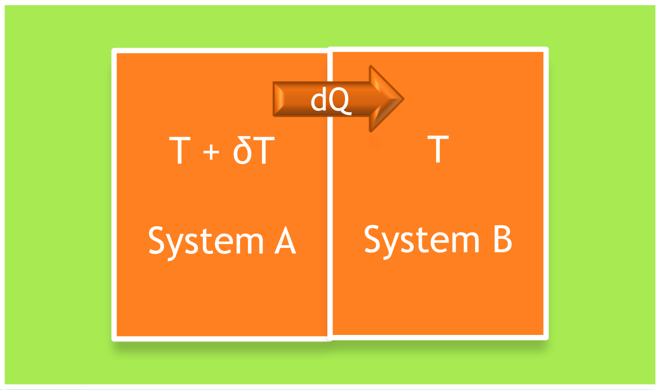
Energy stored in the droplet and then the metal is dispersed as more alcohol vapor is produced

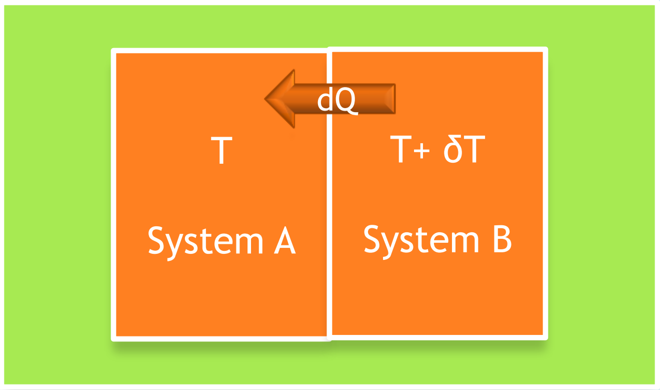


The amount of energy in the system is the same, but it spreads out, becomes less concentrated, or disperses

Entropy is the measure of energy dispersal

Consider two isolated systems in thermal contact and at nearly the same temperature


dQ
T + δT
T
System A
System B


dQ
T
T+ δT
System A
System B

A small change in temperature can reverse the direction of heat flow

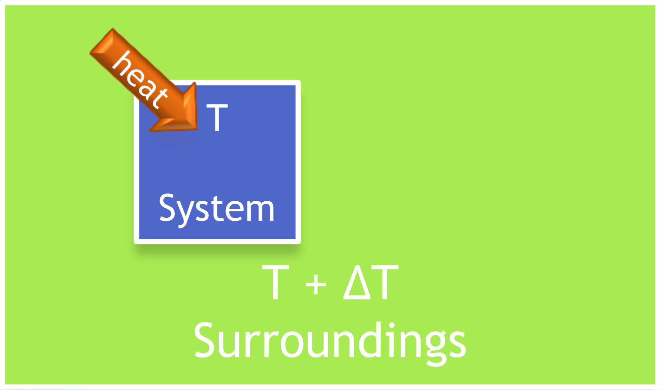
$$\Delta S = \Delta S_A + \Delta S_B = 0$$

Entropy of a system undergoing a reversible process does not change

Systems A and B are isolated from the surroundings by an adiabatic barrier

Real processes take place in systems in contact with the surroundings
So the entropy of the surroundings should be taken into account for spontaneity considerations

Consider a glass of cold water in a hot room



Energy dispersion towards lower thermal equilibrium

$Q_{surroundings} < 0$, $Q_{system} > 0$, same magnitude of heat transferred

$\Delta S_{sys} > 0$, $\Delta S_{surr} < 0$ entropy of water increased
entropy of room decreased

$Q_{surroundings} + Q_{system} = 0$

$$\left|\frac{Q_{surr}}{T_{surr}}\right| < \left|\frac{Q_{sys}}{T_{sys}}\right|$$

$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr} > 0$

Entropy of universe increases when energy is dispersed in one direction as in spontaneous processes

Entropy of universe stays constant for reversible processes

Entropy of a system or its surroundings may decrease or increase

In any case $\Delta S_{universe} \geq 0$

In macroscopic world entropy and the degree of irreversibility are the same thing
It is easier to understand entropy from a microscopic point of view

Clausius invented the term entropy upon making macroscopic observations
Ludwig Boltzmann described the concept of entropy on the molecular level

$$S = k \log W$$

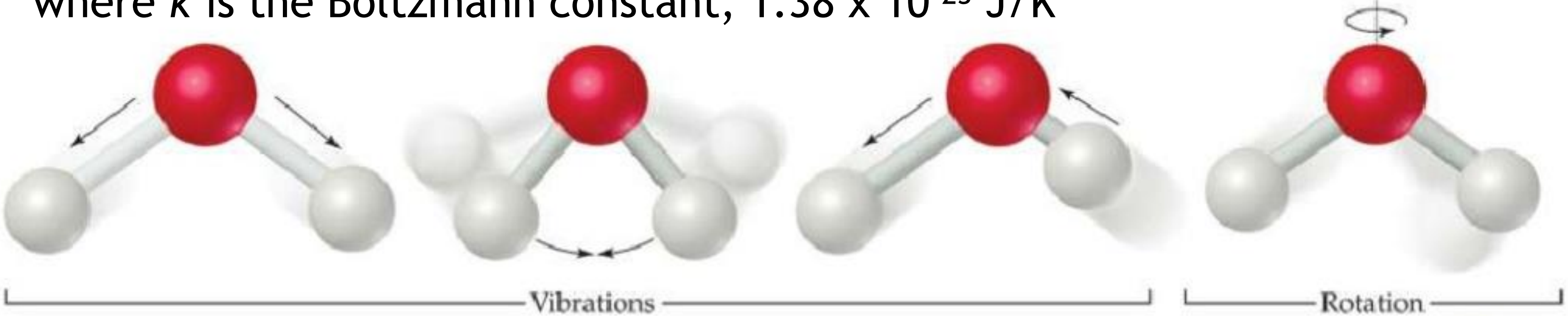
Microstates of matter W, are referred to as the arrangements of a sample of molecules at a particular instant of time

Translational, vibrational and rotational motions of molecules increase with temperature which is a measure of the average kinetic energy of the molecules in a sample

Thus

$$\Delta S = k \ln \frac{W_{final}}{W_{initial}}$$

where *k* is the Boltzmann constant, 1.38 x 10^{-23} J/K



Temperature is a measure of the average kinetic energy of the molecules in a sample

An atom can only move and rotate while molecules can move, vibrate and rotate

Suppose you have an advanced electron microscope and can see a sample of atoms or molecules at an instant of time

The number of different configurations captured by the electron microscope out of 1000 snapshots represent the number of microstates W

$$S = k\ \log W$$

Thus entropy increases with the number of ways energy can be dispersed in a system

Entropy of a system that has only a single microstate has zero entropy

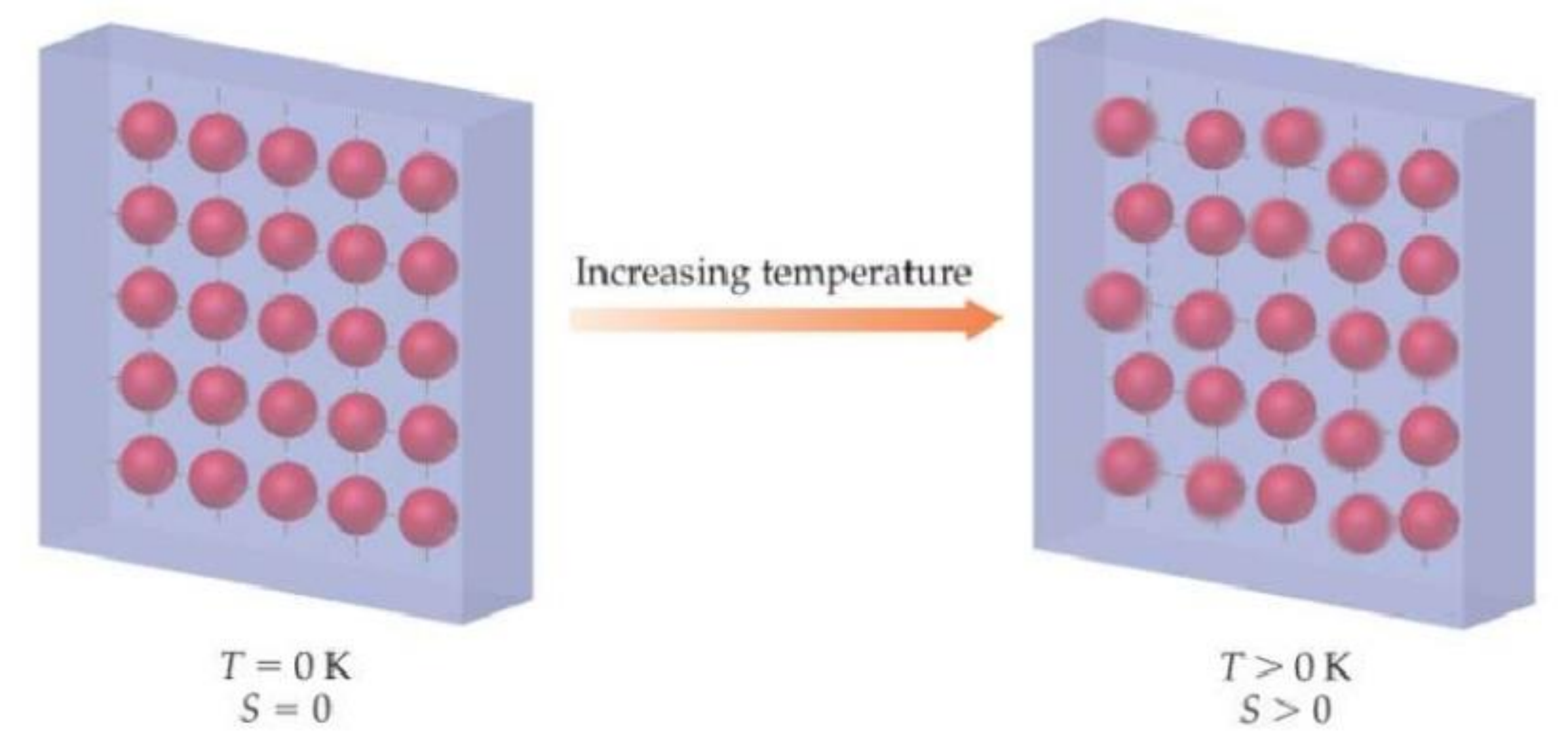
$$S = k\ \log 1 = 0$$

Third law of thermodynamics states that the only substance that has a perfectly ordered state with zero entropy is a perfect crystal at absolute zero

These extreme conditions can never be met, therefore all substances have some entropy or randomness

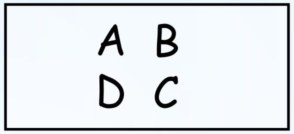
Unlike enthalpy, entropy of an element under standard conditions is defined a value
$\Delta S^o_{298}(H_2(g)) = -130.6$ J/mole.K

Standard entropy change: Entropy change per mole of a substance upon heating from 0 K to 298 K at 1 atm

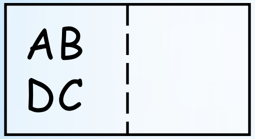


One mole of a substance containing $6*10^{23}$ molecules has an enormous number of microstates

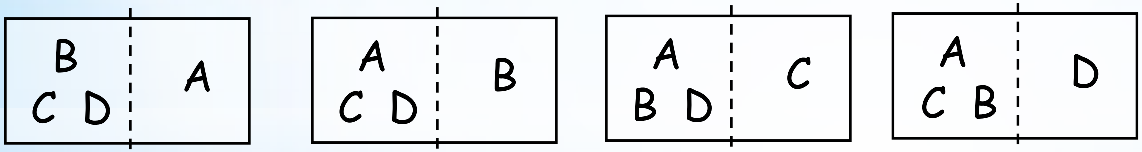
Statistics helps us understand the microstate concept without dealing with large numbers



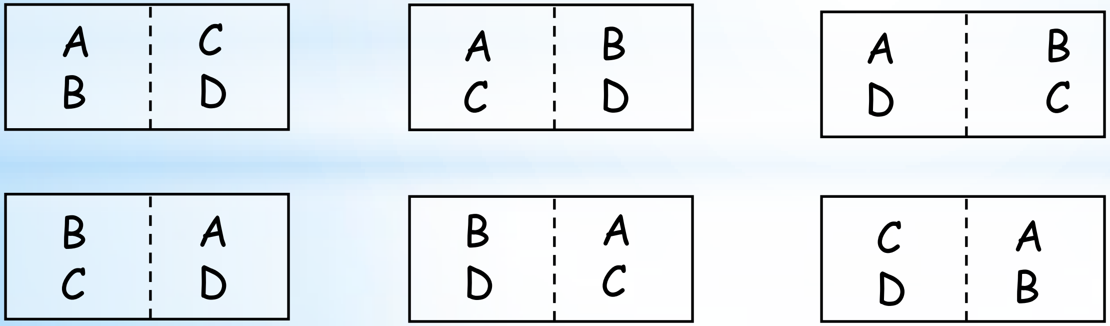
Example – Simple system of a 4-particle gas
Calculate the probability of finding all four particles in the left half of the chamber



1 configuration (microstate)
with 4 particles at left



4 microstates with 3 particles at left

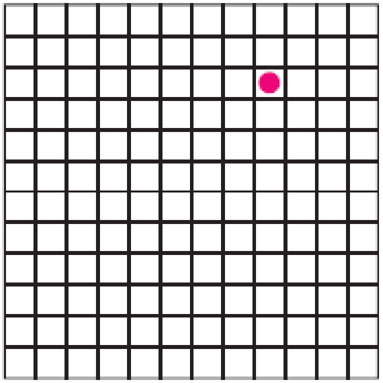


6 microstates with 2 particles at left

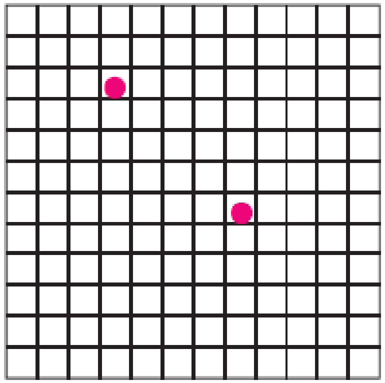
p(4 at left) = 1/16

# particles on the left	0	1	2	3	4	total
# of microstates (w)	1	4	6	4	1	16

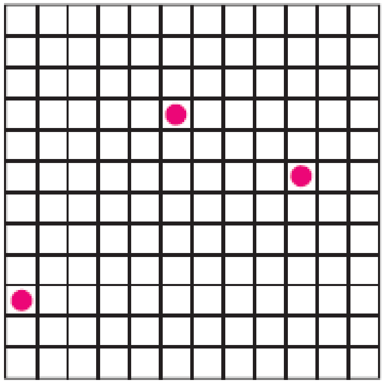
Similarly consider the number of microstates for different number of particles in a chamber with 144 cells



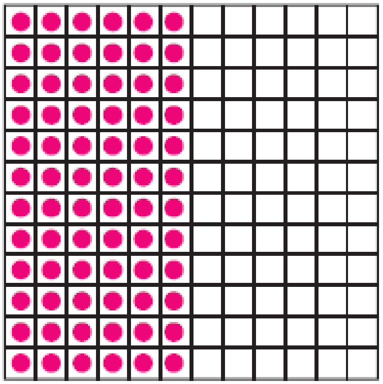
$W = 144$



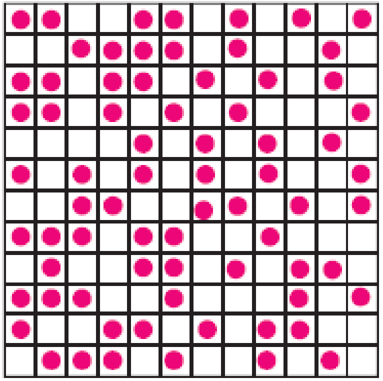
$W = 144 \times 143$



$W = 144 \times 143 \times 142$

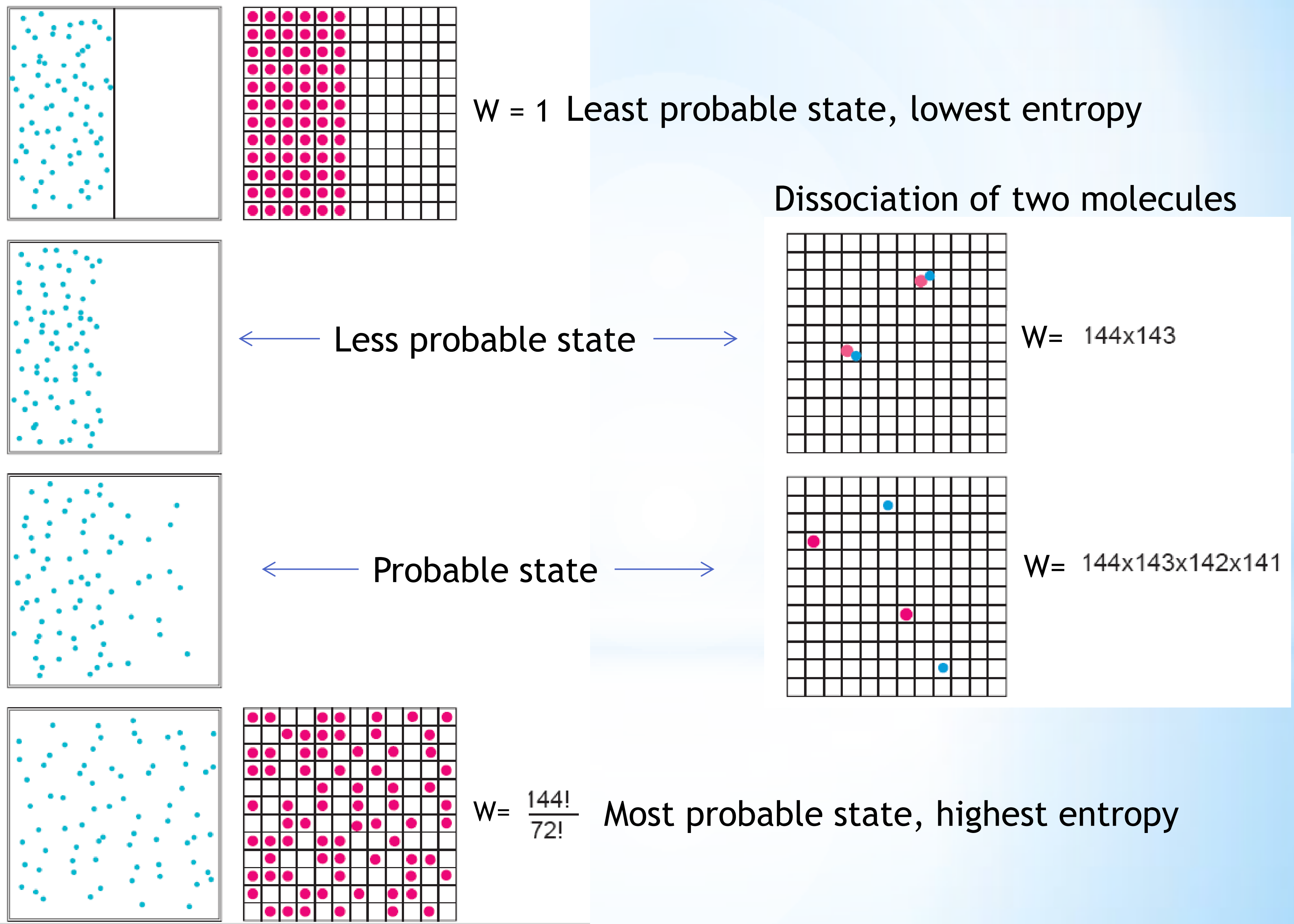


$W = 4$



$$W = \frac{144!}{72!}$$

A gas with 72 particles expanding from the left side to the whole chamber has the following microstates:



W = 1 Least probable state, lowest entropy

Dissociation of two molecules

Less probable state

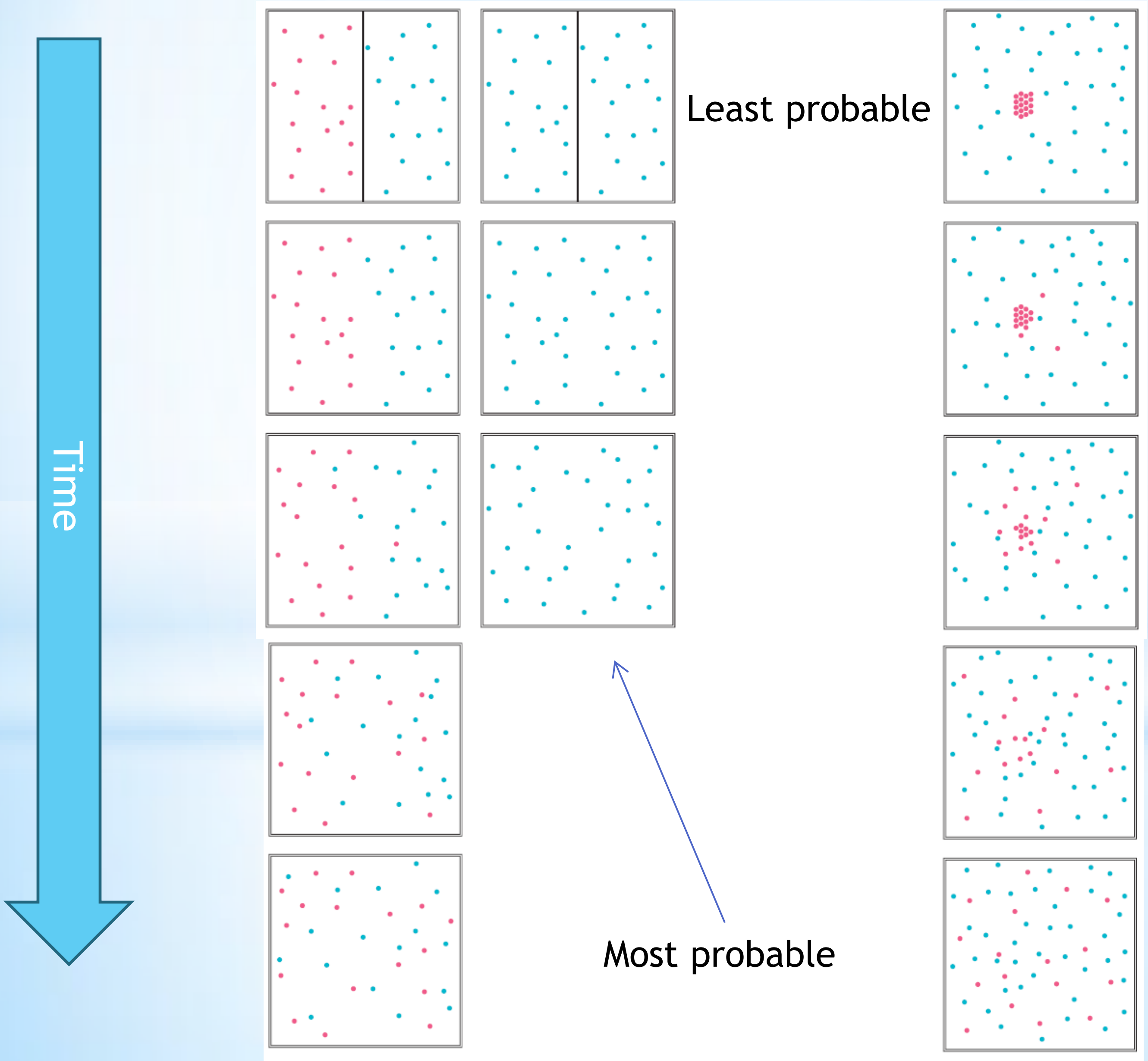
W= 144x143

Probable state

W= 144x143x142x141

W= $\frac{144!}{72!}$ Most probable state, highest entropy

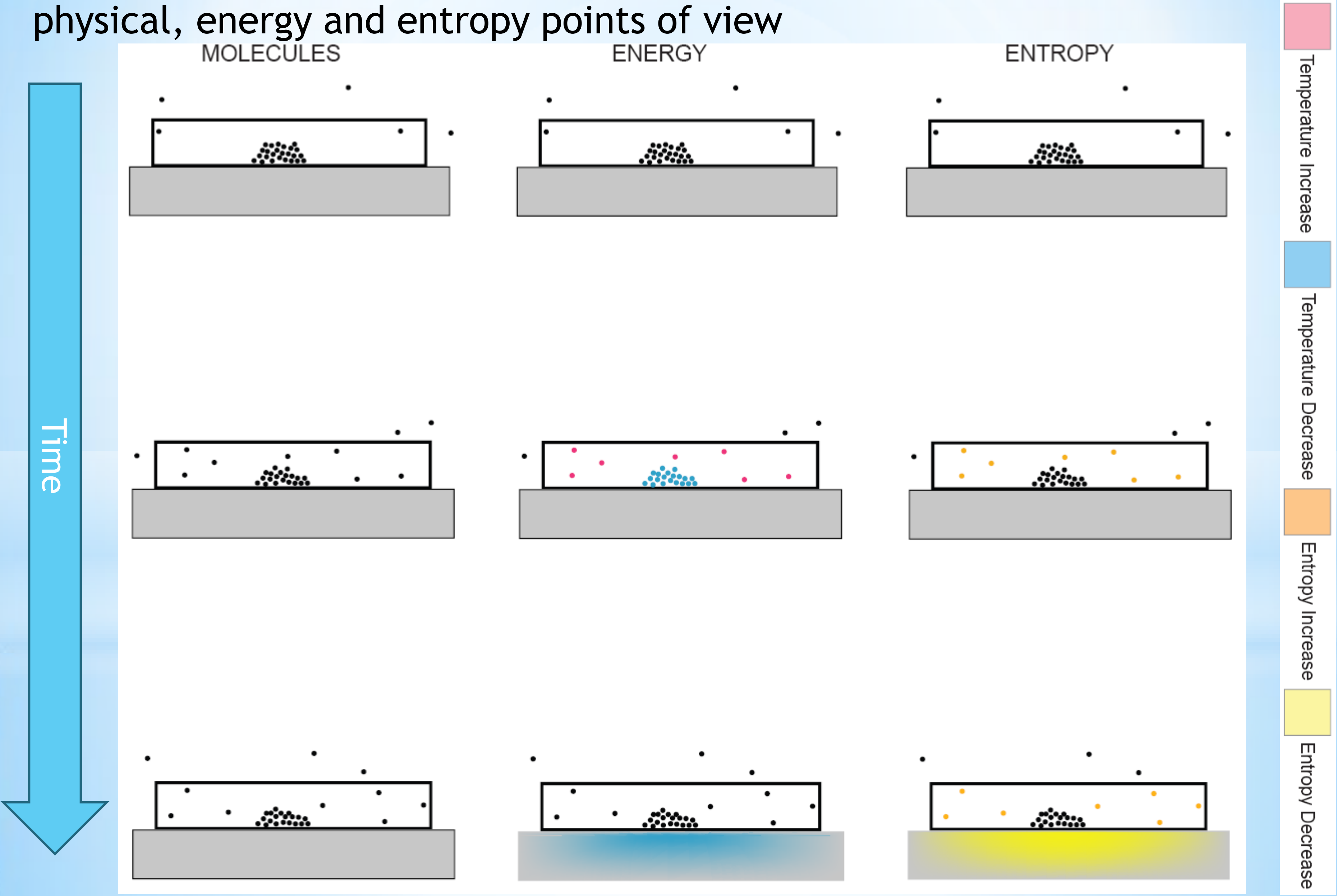
Similarly for mixing of unlike and like gases and dissolution of a solute, the microstates and their probabilities are given as



Least probable

Most probable

Consider a system consisting of a drop of water on a petri dish and the table and air are surroundings. Endothermic evaporation of water is seen from physical, energy and entropy points of view



Entropy calculations for reversible processes

If a system absorbs heat in any sort of a reversible process, its entropy will increase

$$dS_{sys} = \frac{\partial Q_{rev}}{T}$$

Entropy of the surroundings decreases correspondingly

$$dS_{surr} = \frac{-\partial Q_{rev}}{T}$$

Total entropy change for the universe is zero in a reversible process

$$dS_{uni} = dS_{sys} + dS_{surr}$$

For constant pressure path

$$\Delta S_{sys} = \int_{S_1}^{S_2} dS_{sys} = \int_{T_1}^{T_2} \frac{dH_{rev}}{T} = n\int_{T_1}^{T_2} \frac{C_p}{T} dT$$

For constant volume path

$$\partial Q_{rev} = dU,\ dU = C_v dT$$

$$\Delta S_{sys} = \int_{S_1}^{S_2} dS_{sys} = \int_{T_1}^{T_2} \frac{dU_{rev}}{T} = n\int_{T_1}^{T_2} \frac{C_v}{T} dT$$

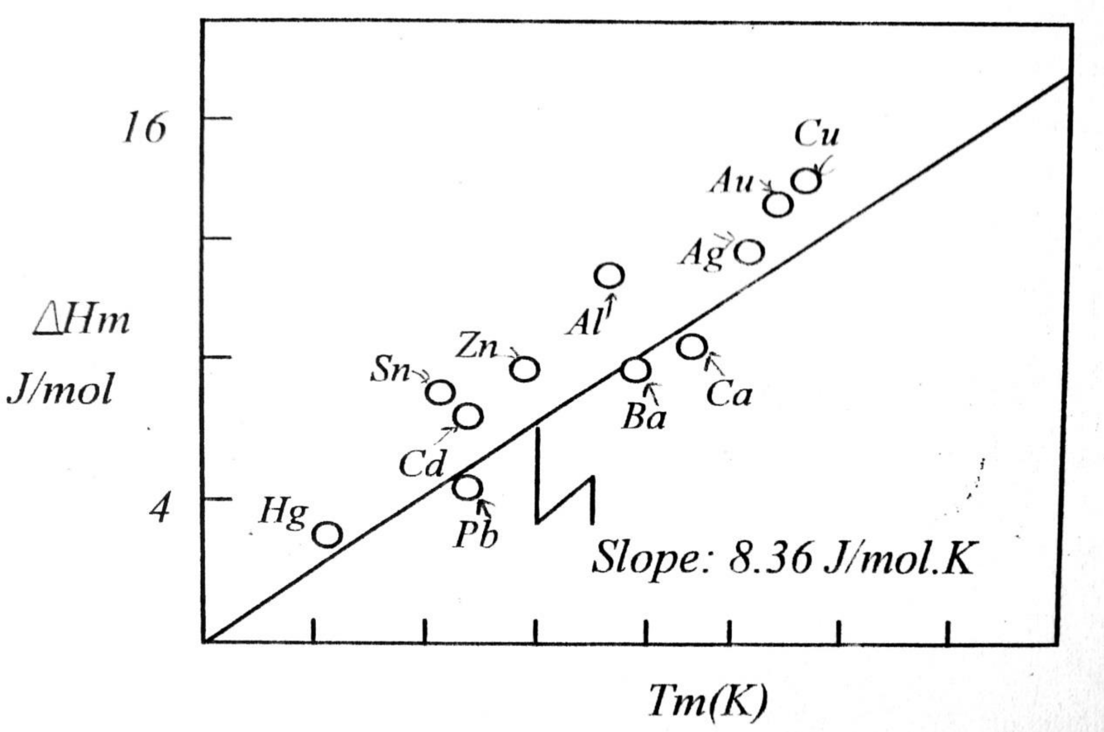
Entropy calculations for reversible phase transformation

Phase transformations occur at constant temperature

$$\Delta S_{tr} = \frac{Q_{tr}}{T_{tr}}$$

Entropy change for phase transformations occuring at constant temperature

$$\Delta S_{tr} = \frac{\Delta H_{tr}}{T_{tr}}$$



A plot of ΔH_m vs T_m for metals indicates that $\Delta H_m/T_m$ lies in the vicinity of 2 calories/mole.K

Richard’s rule

$$\Delta S_m = \frac{\Delta H_m}{T_m} = 2\,\frac{cal}{mole.K}$$

$$= 8.36\,\frac{J}{mole.K}$$

Entropy of melting is approximately the same for all solids

Similarly a plot of ΔH_v vs T_v for metals indicates that $\Delta H_v/T_v$ lies in the vicinity of 21 calories/mole.K

$$\Delta S_v = \frac{\Delta H_v}{T_b} = 21\frac{cal}{mole.K} = 87.78\frac{J}{mole.K}$$

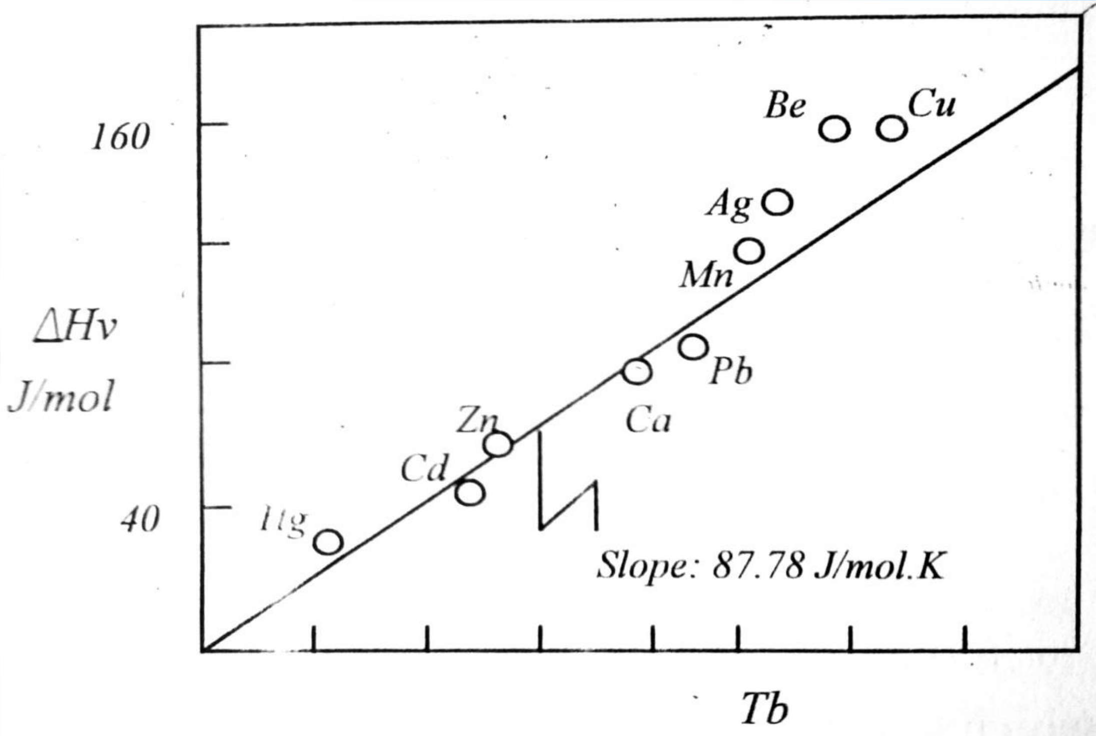
This correlation known as Trouton's rule states that entropy of metals with relatively low boiling points are approximately the same

The relation is used to estimate ΔH_v for a substance with known boiling T

Example – Boling point for lead is 2024 K. Estimate the latent heat of evaporation

$\Delta H_v = \Delta S_v \, . \, T_b$
= (87.78)(2024)
= 177667 J/mole

Measured ΔH_v = 179496 J/mole



Entropy change with temperature involving reversible phase transformations at 1 atm

Entropy change for heating 1 mole of a substance is

$$S_2 - S^o{}_{298} = \int_{298}^{T_2} \left(\frac{C_p}{T}\right) dT$$

$$S_2 = S^o{}_{298} + \int_{298}^{T_2} \left(\frac{C_p}{T}\right) dT$$

- $T_2 < T_m$

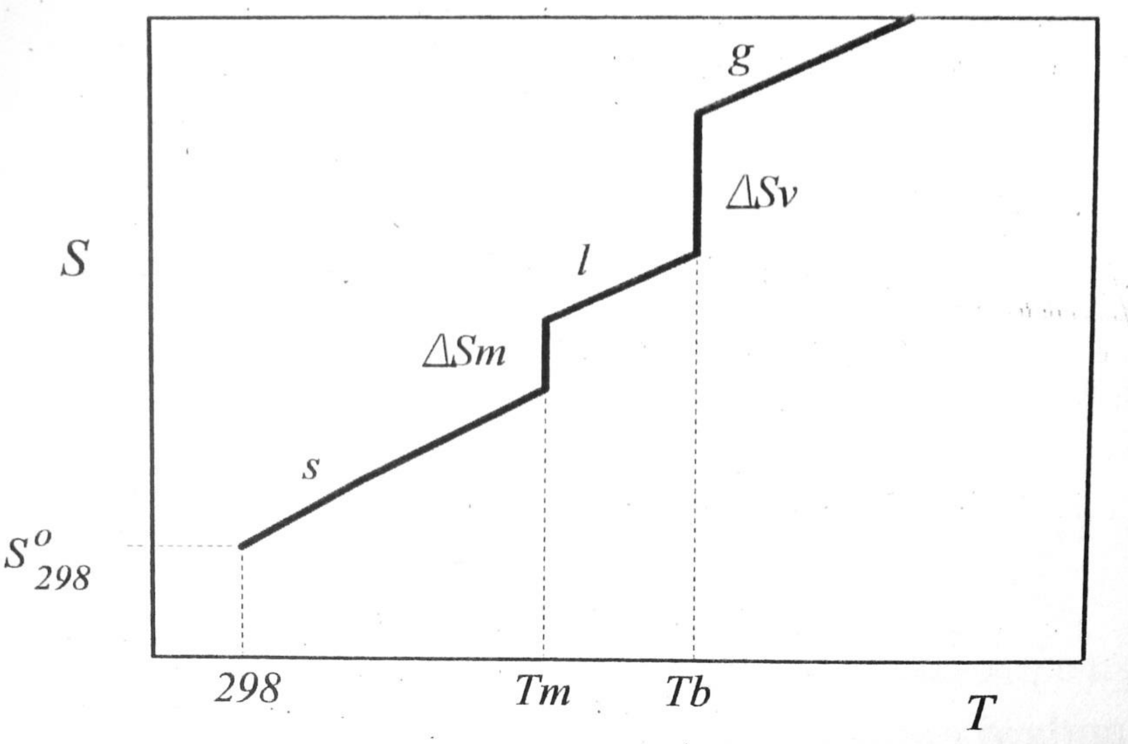
$$\Delta S = \int_{T_1}^{T_2} \left(\frac{C_p(s)}{T}\right) dT$$

- $T_1 < T_m < T_2 < T_b$

$$\Delta S = \int_{T_1}^{T_m} \left(\frac{C_p(s)}{T}\right) dT + \frac{\Delta H_m}{T_m} + \int_{T_m}^{T_2} \left(\frac{C_p(l)}{T}\right) dT$$

- $T_1 < T_m < T_2 > T_b$

$$\Delta S = \int_{T_1}^{T_m} \left(\frac{C_p(s)}{T}\right) dT + \frac{\Delta H_m}{T_m} + \int_{T_m}^{T_b} \left(\frac{C_p(l)}{T}\right) dT + \frac{\Delta H_v}{T_b} + \int_{T_b}^{T_2} \left(\frac{C_p(g)}{T}\right) dT$$



Example - Calculate the entropy change of magnesium when it is heated from room temperature to 1000 °C

Substance	ΔH^o (kJ/mol)	S^o (J/mol.K)	C_P (J/mol.K)	ΔH_m (J/mol)
Mg (s)		32.53	$25.7+0.00625T+327000/T^2$	9040@ 923 K
Mg (l)		34.46	30.98	

Entropy calculations for irreversible phase change at 1 atm

Transformations taking place at temperatures other than equilibrium transformation points are irreversible transformations

$$\Delta S_{a-b-c} = \Delta S_{a-d-c}$$

$$\Delta S_{a-b} + \Delta S_{b-c} = \Delta S_{a-d} + \Delta S_{d-c}$$

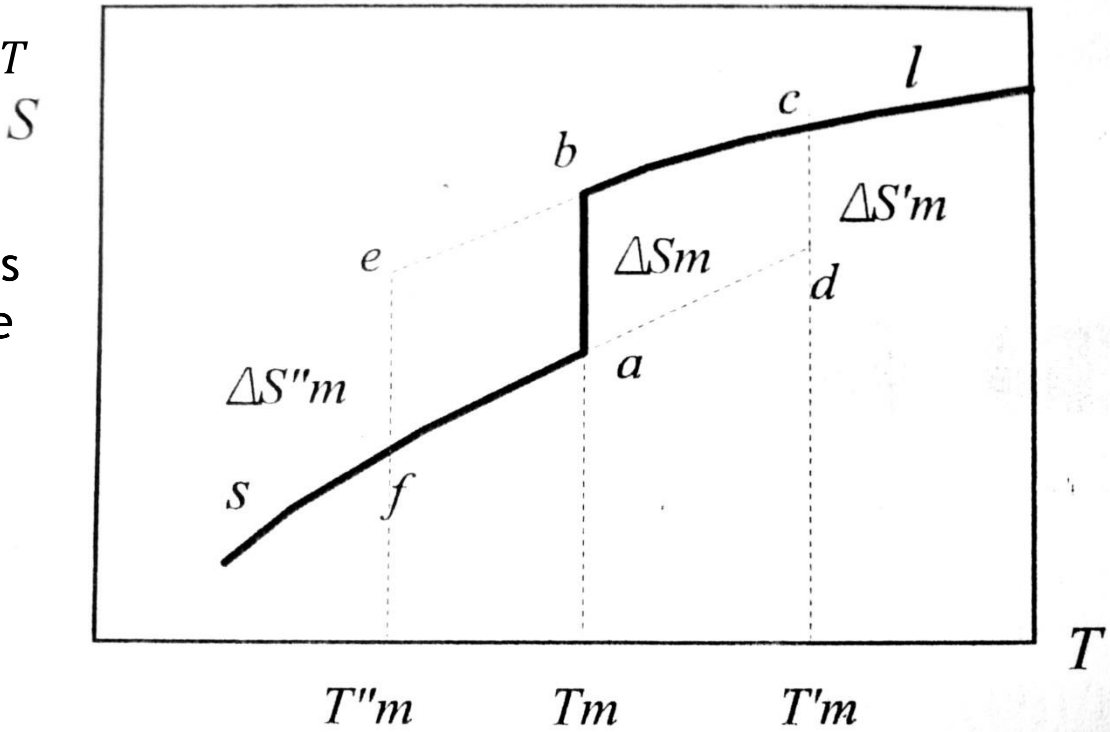
$$\Delta S_m + \int_{Tm}^{T'm} \frac{C_P(l)}{T} dT = \int_{Tm}^{T'm} \frac{C_P(s)}{T} dT + \Delta S'_m$$

$$\Delta S'_m = \Delta S_m + \int_{Tm}^{T'm} \frac{(C_P(l) - C_P(s))}{T} dT$$

Entropy change of the system

Entropy change of the surroundings is calculated using the enthalpy change for the system:

$$\Delta S_{surr} = \frac{\Delta H'_m}{T'_m}$$



Example - The normal freezing point for pure copper is 1083 °C but small droplets of liquid copper have been supercooled to 847 °C before spontaneous solidification occurs. Calculate the entropy change for the spontaneous solidification of copper at 847 °C

Substance	ΔH^o (kJ/mol)	S^o (J/mol.K)	C_P (J/mol.K)	ΔH_m (J/mol)
Mg (s)		32.53	$25.7+0.00625T+327000/T^2$	9040@ 923 K
Mg (l)		34.46	30.98	
Cu (s)		33.36	$22.65+0.00628T$	13000 @ 1356 K
Cu (l)		41.62	31.40	

Standard entropy of a reaction is calculated in the same way as standard enthalpy

$$\Delta S^{o} = \sum n\Delta S^{o}{}_{products} - \sum m\Delta S^{o}{}_{reactants}$$

Entropy usually increases for

- A reaction in which a molecule is broken into two or more smaller molecules
- A reaction in which there is an increase in the number of moles of a gas
- A process in which a solid changes to a liquid or gas or a liquid changes to a gas

Example – Calculate the entropy change of the reaction

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

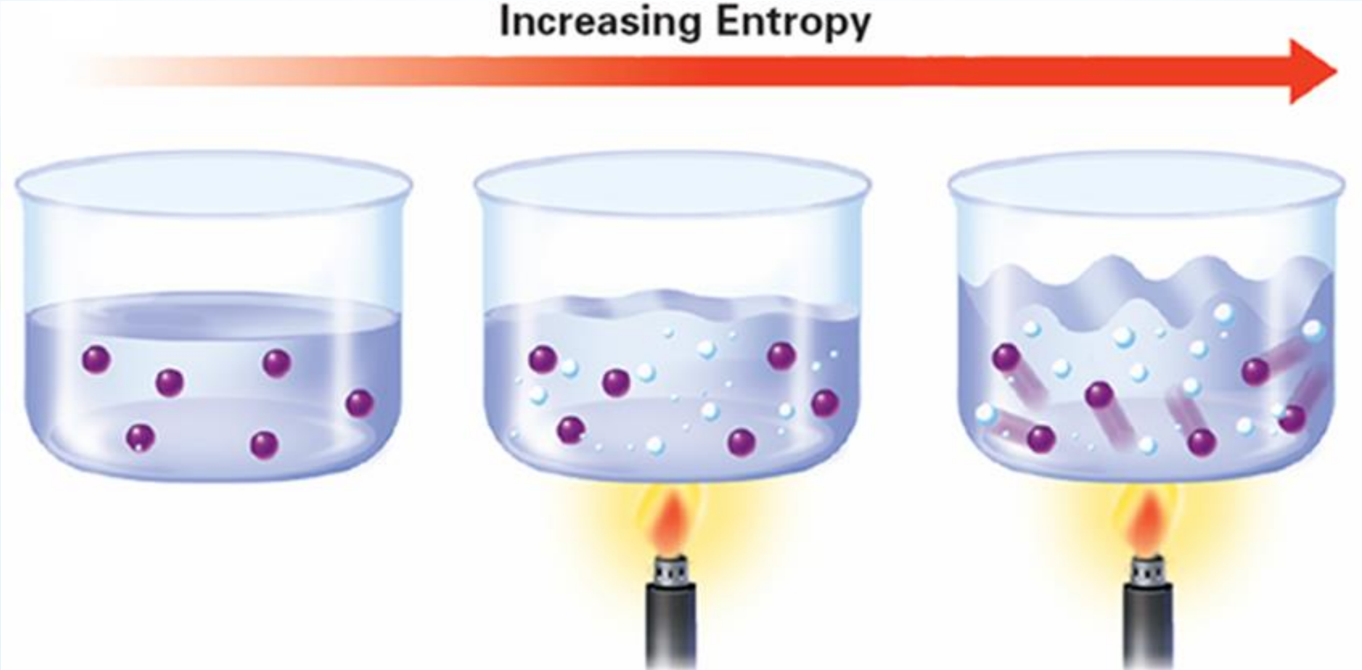
$S^{o}_{298}(NO(g))$ = 211J/mole.K
$S^{o}_{298}(O_2(g))$ = 205 J/mole.K
$S^{o}_{298}(NO_2(g))$ = 240 J/mole.K

A system evolves spontaneously toward the state with

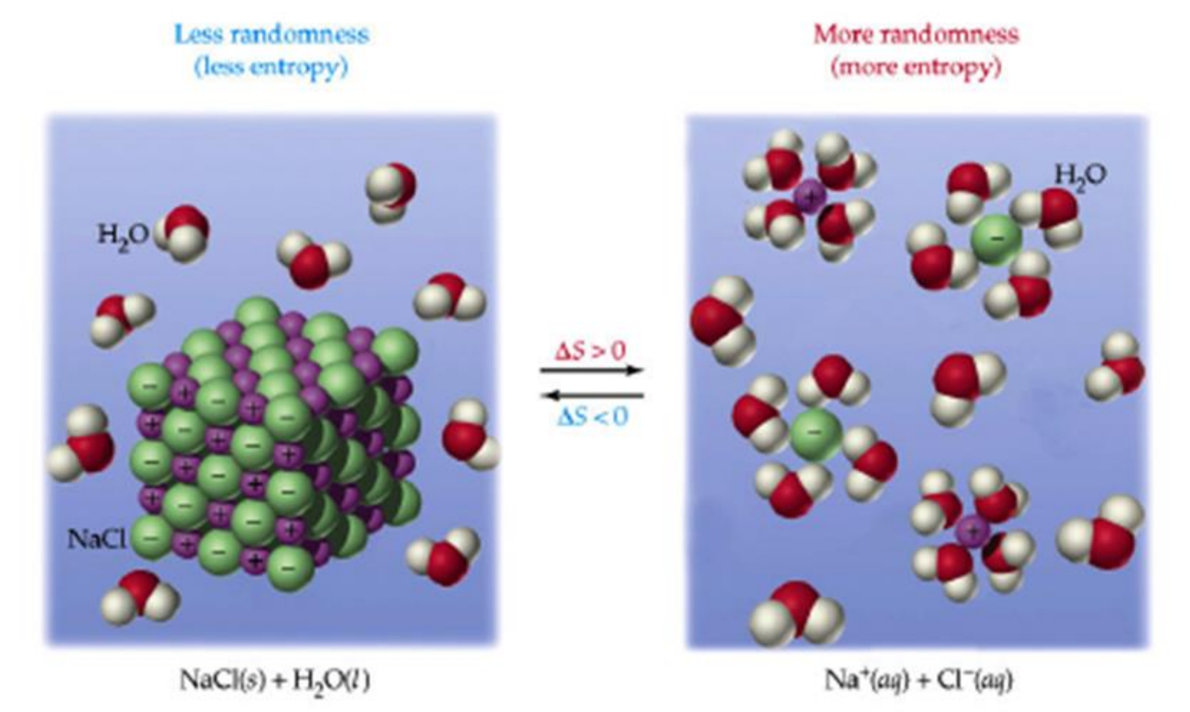
- most microstates *W*
- greatest disorder
- largest entropy

$$S = k\,\log W$$

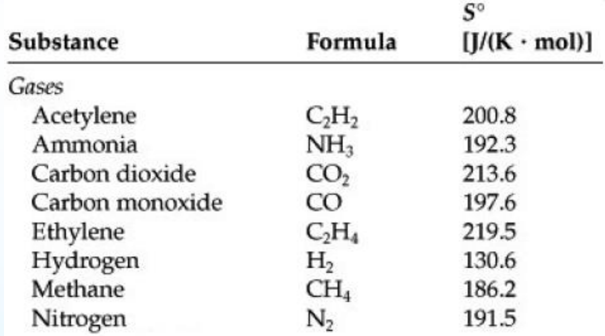
In general entropy increases with the freedom of motion of the molecules, so is proportional to temperature, volume, number and complexity of independently moving molecules
Entropy is most closely related with temperature
Molecules rotate and move faster at higher T resulting in higher disorder and entropy



Greater number of products formed in a reaction results in higher entropy
Example – Dissolution of salt in water $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

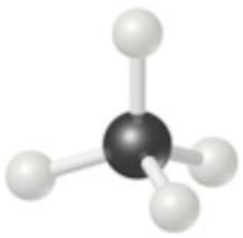


Example – Consider the reaction $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$

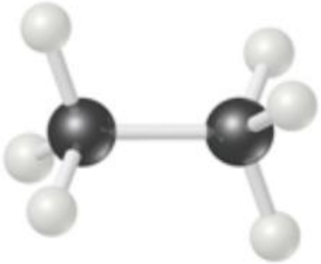


Substance	**Formula**	**$S°$ [J/(K · mol)]**
Gases		
Acetylene	C_2H_2	200.8
Ammonia	NH_3	192.3
Carbon dioxide	CO_2	213.6
Carbon monoxide	CO	197.6
Ethylene	C_2H_4	219.5
Hydrogen	H_2	130.6
Methane	CH_4	186.2
Nitrogen	N_2	191.5

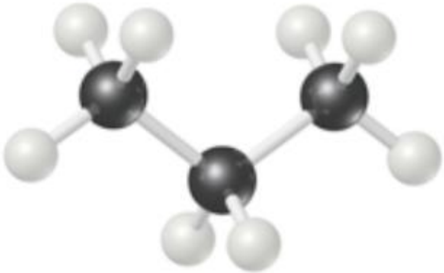
Formation of more complex molecules with more rotational and vibrational states is favored by entropy increase



Methane, CH_4
$S° = 186.3\ J\ mol^{-1}\ K^{-1}$



Ethane, C_2H_6
$S° = 229.6\ J\ mol^{-1}\ K^{-1}$



Propane, C_3H_8
$S° = 270.3\ J\ mol^{-1}\ K^{-1}$

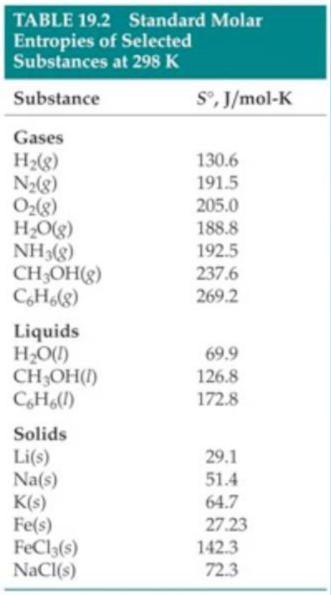
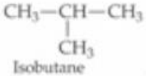


TABLE 19.2 Standard Molar Entropies of Selected Substances at 298 K

Substance	S°, J/mol-K
Gases	
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
Liquids	
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
Solids	
$Li(s)$	29.1
$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

Example – Which compound has the highest entropy at liquid state?

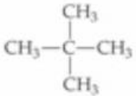
$CH_3CH_2CH_2CH_3$
Butane
mp −135° C
bp −0.5° C



$\mathrm{CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}CH_3}$

Isobutane
(2-methylpropane)
mp −145° C
bp −10° C

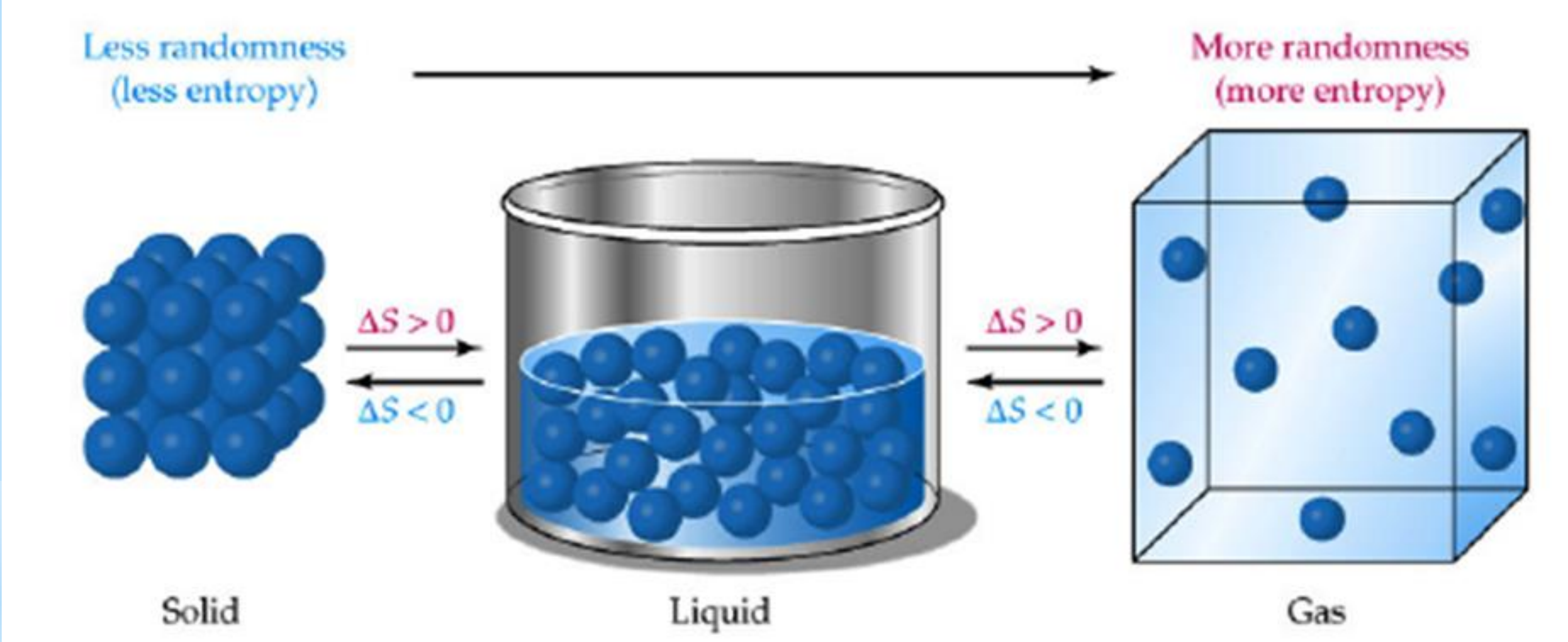
$CH_3CH_2CH_2CH_2CH_3$
Pentane
mp −130° C
bp +36°C



$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}}{-}CH_3}$

Neopentane
(2,2-dimethylpropane)
mp −20° C
bp +9° C

The state of matter with the greatest entropy is gas
Entropy of a substance increases with phase change from the least disordered solid state to gas



Example – Melting of an ice cube at constant temperature and atmospheric pressure

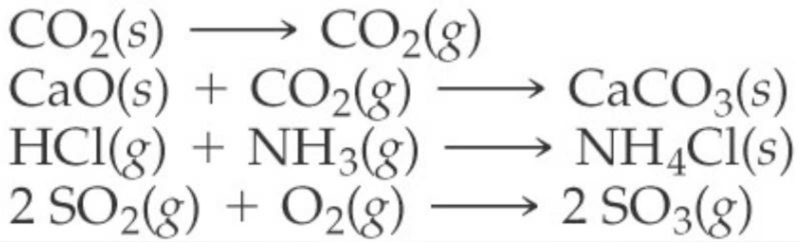
$$H_2O(s) \rightarrow H_2O(l)$$

Example – Oxidation of iron $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

Processes that are spontaneous at one temperature may be non-spontaneous at other

Examples

Estimate the entropy change of the following reactions proceeding in the forward direction



$$CO_2(s) \longrightarrow CO_2(g)$$
$$CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$$
$$HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$$
$$2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$$

Choose the sample of matter that has greater entropy in each pair:

a) 1 mole NaCl(s) or 1 mole HCl(g) at 25 C
b) 2 moles HCl(g) or 1 mole HCl(g) at 25 C
c) 1 mole HCl(g) or 1 mole Ar(g) at 25 C

Choose the substance that has greater entropy in each case:

a) 1 mole H_2(g) at STP or 1 mole H_2(g) at 100 C and 0.5 atm
b) 1 mole H_2O(s) at 0 C or 1 mole H_2O(l) at 25 C
c) 1 mole H_2(g) at STP or 1 mole SO_2(g) at STP
d) 1 mole N_2O_4(g) at STP or 1 mole NO_2(g) at STP

Which process will result in a decrease in entropy?

a) Dissolving NaCl in water
b) Melting ice
c) Falling leaves
d) Oxidation of iron
e) Decomposition of H_2O to H_2 and O_2

Entropy is not the only criterion for spontaneity

$\Delta S^o_{298}(NH_4Cl(g))$ = 94.85 J/mole.K
$\Delta S^o_{298}(NH_3(g))$ = 192.3 J/mole.K
$\Delta S^o_{298}(HCl(g))$ = 186.9 J/mole.K

Consider the reaction $NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$

The reaction is not spontaneous at standard conditions!
Reverse reaction is spontaneous

Enthalpy of the reaction should also be taken into account

$\Delta H^o_{298}(\text{Total})$ = 176 kJ/mole whereas $\Delta S^o_{298}(\text{Total})$ = 284 J/mole.K

Heat that flows into the system decreases the entropy of the surroundings

$$S_{surroundings} = \frac{-Q_{system}}{T}$$

For an isothermal and constant pressure process,

$$S_{surroundings} = \frac{-\Delta H_{system}}{T}$$

Entropy of the surroundings always decreases with heat flow into the system
Entropy of the surroundings always increases with exothermic reaction in the system

Example - A box with five adiabatic sides contains an ideal gas with an initial temperature T_0. The sixth side is diathermal and is placed in contact with a reservoir with a constant temperature $T_2 > T_0$. Assuming the specific heat capacity of the system does not change with temperature, why must the entropy change of the universe always be increasing as the box warms?

a) Entropy will always be increasing since the work done on the gas in the box is negative.
b) Entropy will always be increasing since the temperature of the box is always less than or equal to T_2.
c) Entropy will always be increasing since this process is reversible.
d) Entropy will always be increasing since the temperature of the box is always greater than absolute zero

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

$$\Delta S_{universe} = \Delta S_{system} + \frac{-\Delta H_{system}}{T}$$

The ultimate criterion for spontaneity of a process is that the entropy of universe should increase

$$\Delta S_{universe} = \Delta S_{system} + \frac{-\Delta H_{system}}{T} > 0$$

Multiplying both sides by -T gives the spontaneity equation:

$$-T\Delta S_{universe} = \Delta H_{system} - T\Delta S_{system} < 0$$

$$T\Delta S_{universe} > 0$$

$-T\Delta S_{universe}$ is called the **Gibbs free energy of the system**

For a process to be spontaneous, entropy of the universe should increase and Gibbs free energy of the system should decrease

Example – Calculate the Gibbs free energy for the reaction at 298 K What effect will increasing the temperature have on spontaneity?

$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$

$\Delta S^o_{298}(NH_4Cl(g))$ = 94.9 J/mole.K
$\Delta S^o_{298}(NH_3(g))$ = 192.3 J/mole.K
$\Delta S^o_{298}(HCl(g))$ = 186.9 J/mole.K
$\Delta H^o_{298}(NH_4Cl(g))$ = -314.5 kJ/mole
$\Delta H^o_{298}(NH_3(g))$ = -46.2 kJ/mole
$\Delta H^o_{298}(HCl(g))$ = -92.3 kJ/mole