The second law of thermodynamics

The second law of thermodynamics → the entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.

- ❖ The entropy change in the universe (ΔS_{univ}) for any process is the sum of the entropy changes in the system (ΔS_{sys}) and in the surrounding.
- ✓ ΔS universe must be greater than zero.
- ✓ It doesn't place restriction on either ΔS sys or ΔS_{surr}.
- ✓ It's possible for either ΔS_{sys} or ΔS_{surr} to be negative.

$$\therefore \Delta Suniv = \Delta S\ sys + \Delta Ssurr > 0$$

For an equilibrium process:

- ✓ ΔS_{univ} is zero.
- ✓ ΔS_{sys} and ΔS_{surr} must be equal in magnitude, but opposite in sign.

$$\therefore \Delta Suniv = \Delta S\ sys + \Delta Ssurr = 0$$

Entropy changes in the system

❖ To calculate ΔS_{univ} , we need to know both " ΔS_{sys} and ΔS_{surr}".

To know ΔS_{sys}

→Suppose that the system is represented by the following reaction.

$$aA + bB \rightarrow cC + dD$$

∴The standard entropy of reaction ΔS°rxn

$$\Delta S^{\circ}_{rxn} = [cS^{\circ}(C) + dS^{\circ}(D)] - [aS^{\circ}(A) + bS^{\circ}(B)]$$

In general

$$\Delta S^{\circ}_{rxn} = \sum nS^{\circ}(product) - \sum mS^{\circ}(reactants)$$

$\sum$ → represent summation in the reaction

m , n → Stoichiometric Coefficients

The standard entropy Value for a large number of compound have been measured in J/k.mol

Note

$$\Delta S^{\circ}_{rxn} = \Delta S_{sys}$$

Example 1:

From the standard entropy values, calculate the standard entropy changes for the following reactions at 25ºC

a) $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2\,(g)}$

$\Delta S^{o}_{rxn} = [S°(Cao) + S°(CO2)] - [S°(CaCO3)]$

$= [39.8 + 213.6] - [92.9] = \frac{160.5J}{K.mol}$

b) $N_{2(g)} + 3H_{2(g)} \rightarrow 2\ NH3_{(g)}$

$\Delta S^{o}rxn =$

$[2\ S°(NH3)] - [S°(N2) + 3S°(H2)]$

$= [2 * 193] - [192 + (3 * 131)] = \frac{-199J}{K.mol}$

c) $H_{2(g)} + Cl_2 \rightarrow 2HCl(_{g})$

$\Delta S^{o}rxn = [2S°(HCl)] - [S°(H2) + S°(Cl2)]$

$= [2 * 187] - [131 + 223] = \frac{20J}{K.mol}$

❖There are some general rules

- ✓ If a reaction produces more gas molecules than it consumes.

  ∴ ΔS is positive.

- ✓ If The total number of gas molecules diminishes.

  ∴ ΔS is negative.

- ✓ If There is net change in the total number of gas molecules.

  ∴ $\Delta S°$ may be positive or negative, but will be ralatively small numerically.

- ✓ gases invariably have greater entropy than liquid and solid.
- ✓ For reactions involving only liquid and solid predicting the sign of ΔS^o is more difficult.

Example 2:

Predict whether the entropy change of the system in each of the following reactions is positive or negative.

a) $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(L)}$

- ❖ Two reactant molecules combine to form one product molecule.
- ❖ gases are converted to liquid.

∴ number of microstates will be diminished and hence ΔS° is negative.

b) $NH_4Cl_{(s)} \rightarrow NH_{3(g)} + HCl_{(g)}$

- ❖ a solid is converted to two gaseous products.

∴ ΔS is positive.

c) $H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$

- ❖ The same number of molecules is involved in the reactants as in the product.

all molecules are diatomic.

So, we can't predict the sign of ΔS°.

Entropy changes in the surroundings

To calculate ΔS_{surr}

Exothermic

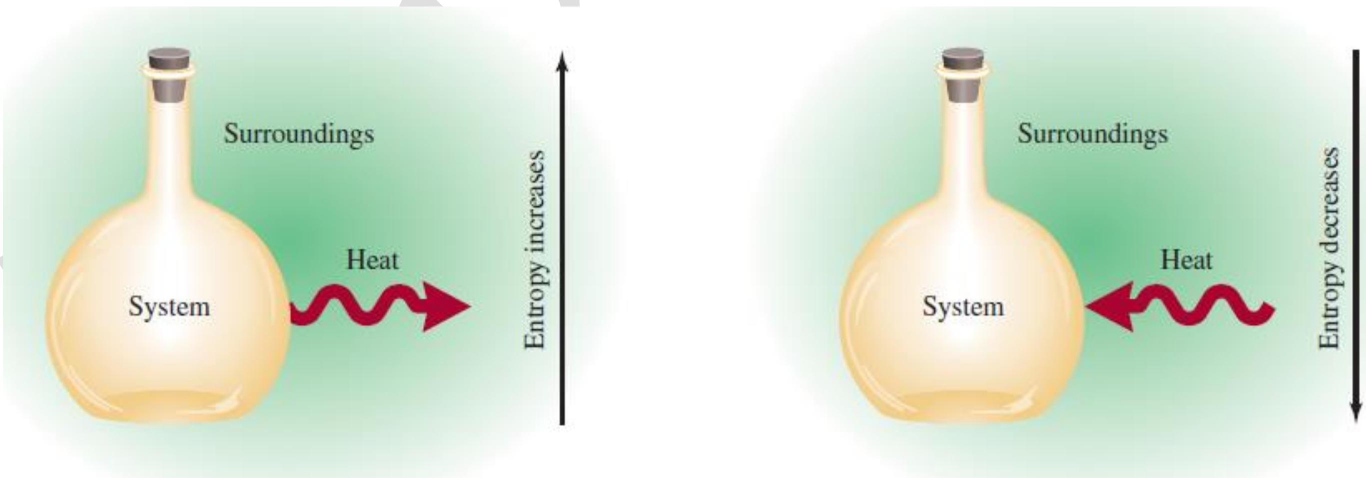
- ✓ heat transferred to the surroundings.
- ✓ There is an increase in the number of microstates.

∴ entropy of the surroundings increase.

Endothermic

- ✓ system absorbs heat from the surroundings.
- ✓ There is decrease in the number of microstates.

∴ entropy of the surroundings decrease.



(a) (b)

- For a constant- pressure processes
- ✓ The heat change is equal to the enthalpy change of the system.
- ✓ The change in entropy of the surroundings is proportional to ΔH_{sys}.

$$\Delta S_{surr} \alpha - \Delta H_{sys}$$

If the process is exothermic → ΔH_{sys} is negative.

→ ΔS_{surr} is positive.

and this indicating an increases in entropy.

If the process is endothermic → ΔH_{sys} is positive.

→ ΔS_{surr} is negative.

and this ensures that the entropy of the surrounding decreases.

Note that:

- The change in entropy for a given amount of heat absorbed also depends on the temperature.
- From the inverse relationship between ΔSsurr and temperature T " in Kelvins" that is, The higher the temperature , The smaller the ΔSsurr and Vice versa , we can rewrite the above relationships as:

$$\Delta Ssurr = \frac{-\Delta sys}{T}$$

Example 3 :

Calculate ΔS_{sys} and ΔS_{surr} to the synthesis of ammonia and wheather the reaction is spontaneous at 25°C

$N_{2(g)} + 3H_2 \rightarrow 2NH_{3(g)}$ ΔH^o_{rxn} = - 92.6KJ/mol

$\Delta S^o_{rxn} = \Delta S_{sys}$

$\therefore \Delta S°rxn = [2S°(NH3)] - [S°N2 + 3S°H2]$

$= [2 * 193] - [192 + 3 * 131]$= - 199J/K.mol

$\therefore \Delta S°rxn = -\frac{199\text{J}}{\text{K}}.\text{mol}$

T= 25+ 273 = 298K

$\Delta Ssurr = \frac{-\Delta sys}{T}$

$\Delta \text{Ssurr} = \frac{-(-92.6 * 1000)}{298}$

$= \frac{311J}{K}.mol$

$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{sur}$

= -199 + 311 = 112J/K.mol

because ΔS_{uni} is positive

∴The reaction is spontaneous at 25°C

The third law of thermodynamics and Absolute entropy

Third Law of thermodynamics → The entropy of a perfect crystalline substance is zero at the absolute zero of temperature.

- ✓ As the temperature increases, the freedom of motion increases and hence also the number of microstates.
- ✓ So, the entropy of any substance at a temperature above 0K is greater than zero.

If the crystal is impure or if it has defects, then its entropy is greater than zero even at 0K.

Absolute entropy of the substance.

When we know the entropy of a pure crystalline substance is zero at absolute zero, we can measure the increase in entropy of the substance when it is heated from 0K to say, 298K

The change in entropy is given by

$$\Delta S = S_f - S_i$$

$$= S_f$$

→ S_f is called the absolute entropy

Why S_f is called absolute entropy?

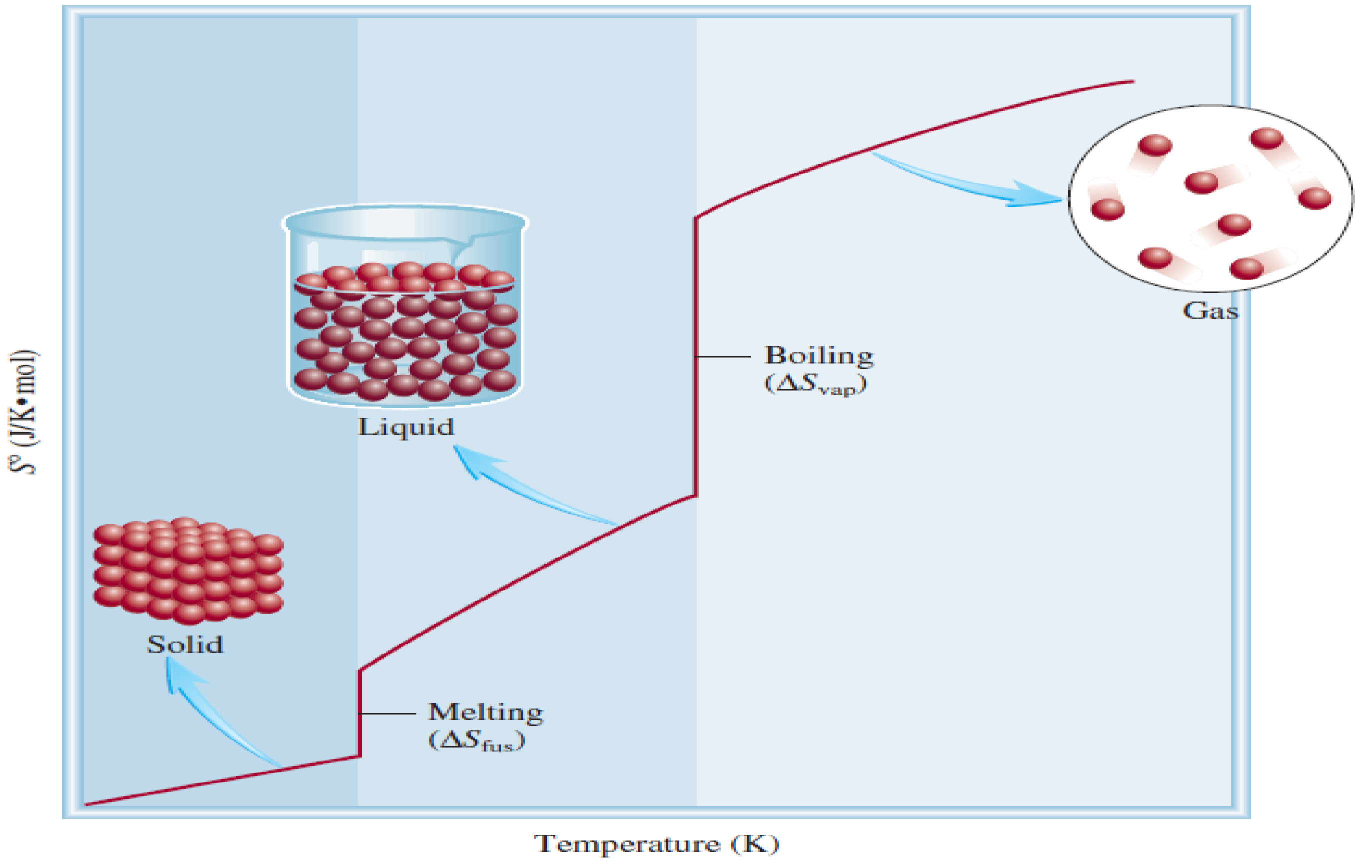
because this is true value and not a value derived using some arbitrary reference.

✓ because measurements are carried out at 1 atm , we usually refer to absolute entropies as standard entropies.

we can't have the absolute energy or enthalpy of a substance?.

because the zero of energy or enthalpy is undefined.

❖ This figure shows the change in entropy of a substance with temperature.



- ✓ **At Absolute zero**, it has a zero entropy value.
- ✓ **As it is heated** , its entropy increases gradually because of greater molecular motion
- ✓ **At the melting point**, There is a Sizeable increase in entropy as the liquid state is formed.
- ✓ **At the boiling point**, There is a large increase in entropy as a result of the liquid-to-vapor transition

Choose

1) The entropy of the universe increase in a spontaneous process and remains unchanged in an equilibrium process this is….

A) First Law of thermodynamics
C) Third Law of thermodynamics
B) Second Law of thermodynamics
D) None of them

2) The entropy of the universe….. in a spontaneous process.

A) increase
C) not change
B) decrease
D) both A and C according to the state.

3) The entropy of the universe……. in an equilibrium process.

A) increase
C) not change
B) decrease
D) both A and C according to the state.

4) For spontaneous process ΔS_{uni} must be……. Zero.

A) greater than
C) equal
B) smaller than
D) all B and C according to the state.

5) For …… process ΔS_{uni} must be greater than Zero.

A) Spontaneous
C) equilibrium
B) nonspontaneous
D) non equilibrium

6) For ………. process the entropy remains unchanged.

A) Spontaneous
C) equilibrium
B) non spontaneous
D) non equilibrium

7) For an equilibrium process.

A) $\Delta S_{uni} = \Delta S_{sys} + \Delta S_{surr} > 0$
C) $\Delta S_{uni} = \Delta S_{sys} - \Delta S_{surr} > 0$
B) $\Delta S_{uni} = \Delta S_{sys} + \Delta S_{surr} = 0$
D) $\Delta S_{uni} = \Delta S_{sys} - \Delta S_{surr} = 0$

8) For Spontaneous process.

A) $\Delta S_{uni} = \Delta S_{sys} + \Delta S_{surr} > 0$
C) $\Delta S_{uni} = \Delta S_{sys} - \Delta S_{surr} > 0$
B) $\Delta S_{uni} = \Delta S_{sys} + \Delta S_{surr} = 0$
D) $\Delta S_{uni} = \Delta S_{sys} - \Delta S_{surr} = 0$

9) The unit of standad entropy for a large number of compound is……

A) J/K.mol
C) J/mol.K
B) J.m /mol
D) J/mol

10) If a reaction produces more gas molecules than it consumes

∴ $\Delta S°$ is … ….

A) Positive
C) Zero
B) Negative
D) Small value

11) If the total number of gas molecules diminished

∴ ΔS° is … ….

A) Positive
B) Negative
C) zero
D) small value

12) If there is no net change in the total number of gas molecules
∴ ΔS° is … …

A) Positive
B) Negative
C) zero
D) both A or B

13) For this reaction $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(L)}$ .The value of entropy….

A) Increase
B) Decrease
C) Not change
D) Can't be predicted

14) For this reaction $NH_4Cl_{(s)} \rightarrow NH_{3(L)} + Hcl_{(g)}$. The value of entropy…….

A) positive
B) Negative
C) Not change
D) Can't be predicted

15) For this reaction $H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$ .The value of entropy….

A) Positive
B) Negative
C) Not change
D) Can't be predicted

16) In exothermic reaction heat transferred to the ……..

A) system
B) Surrounding
C) universe
D) all of the above

17) In endothermic reaction there is…… in the number of microstate.

A) increase
B) Decrease
C) No change
D) None of them

18) The change in entropy for a given amount of heat absorbed also depends on the………

A) Temperature
B) pressure
C) Volume
D) None of them

19) $\Delta S°_{rxn}$ is equal to ……

A) ΔS_{surr}
B) ΔS_{sys}
C) ΔS_{uni}
D) $\Delta H°$

20) ΔS_{surr} is directly proportional to …… and inversely proportional to……..

A) $-\Delta H_{sys}$,T
B) $-\Delta H_{sys}$, P
C) T , ΔH_{sys}
D) P , $- \Delta H_{sys}$

21) The entropy of a perfect crystalline substance is zero at the absolute zero of temperature.

A) First Law of thermodynamic
B) Second Law of thermodynamic
C) Third Law of thermodynamic
D) None of them

22) If the crystal is impure, the entropy is …… zero at 0°K

A) equal
B) greater than
C) Smaller than
D) both A and B

23) Which response includes all the following processes that are accompanied by an increase in entropy?

1. $2SO_2(g) + O_2(g) \rightarrow SO_3(g)$
2. $H_2O(l) \rightarrow H_2O(s)$
3. $Br_2(l) \rightarrow Br_2(g)$
4. $H_2O_2(l) \rightarrow H_2O(l) + (1/2)O_2(g)$

A) 1,2,3,4
B) 1,2
C) 2,3,4
D) 3,4

24) Which response includes all of the following processes that are accompanied by an increase in entropy?

1. $I_2(s) \rightarrow I_2(g)$
2. $2I(g) \rightarrow I_2(g)$
3. $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$
4. $Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$

A) 1,2
B) 1,3
C) 3,4
D) 3

25) Without reference to a table, arrange these reactions according to increasing ΔS.

1. $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$
2. $C(s) + O_2(g) \rightarrow CO_2(g)$
3. $H_2O_2(l) \rightarrow H_2O(l) + (1/2)O_2(g)$

A) 1 < 3 < 2

B) 2 < 3 < 1

C) 2 < 1 < 3

D) 3 < 2 < 1

26) Arrange these reactions according to *increasing* ΔS.

1. $H_2O(g) \rightarrow H_2O(l)$
2. $2NO(g) \rightarrow N_2(g) + O_2(g)$
3. $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$

A) 1 < 2 < 3

B) 2 < 3 < 1

C) 3 < 2 < 1

D) 2 < 1 < 3

27) Determine ΔS° for the reaction $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$.

	S°(J/K·mol)
SO_3	256.2
H_2O	69.9
H_2SO_4	156.9

A) 169.2 J/K·mol

B) 1343.2 J/K·mol

C) -169.2 J/K·mol

D) -29.4 J/K·mol

Solution

ΔS° =[S° (H2SO4)] – [S°(SO3) + S° (H2O)]

ΔS° =[156.9] – [69.9 + 256.2]

= -169.2J/K.mol

28) Calculate ΔS° for the reaction $SO_2(s) + NO_2(g) \rightarrow SO_3(g) + NO(g)$.

	S°(J/K·mol)
$SO_2(g)$	248.5
$SO_3(g)$	256.2
NO(g)	210.6
$NO_2(g)$	240.5

A) 53.6 J/K·mol
B) -53.6 J/K·mol
C) -22.2 J/K·mol
D) 474.8 J/K·mol

Solution

ΔS° =[S° (NO) + S° (SO3)] – [S°(NO2) + S° (SO2)]

ΔS° =[210.6 +256.2] – [240.5 + 248.5]

= -22.2J/K.mol

29) Calculate ΔS° at 25°C for the reduction of PbO(s), $2PbO(s) + C(s) \rightarrow 2Pb(s) + CO_2(g)$ given these absolute entropies:

	S°(J/K·mol)
PbO(s)	69.45
C(s)	5.7
Pb(s)	64.89
$CO_2(g)$	213.6

A) +198.8 J/K·mol
B) +488.0 J/K·mol
C) +353.6 J/K·mol
D) -203.3 J/K·mol

Solution

ΔS° =[S° (CO2) +2S° (Pb)] – [S°(C) + 2S° (Pb)]

ΔS° =[213.6 +2*64.89] – [5.7 + 2*69.45]

= +198.78J/K.mol