Statement of the Third law

- The entropy of a substance varies directly with temperature.
- The lower the temperature, the lower the entropy.
- For example, water above 100ºC at one atmosphere exists as a gas and has higher entropy (higher disorder).
- The water molecules are free to roam about in the entire container. When the system is cooled, the water vapour condenses to form a liquid.

Statement of the Third law

- Now the water molecules are confined below the liquid level but still can move about somewhat freely.
- Thus the entropy of the system has decreased.
- On further cooling, water molecules join together to form ice crystal.
- The water molecules in the crystal are highly ordered and entropy of the system is very low.

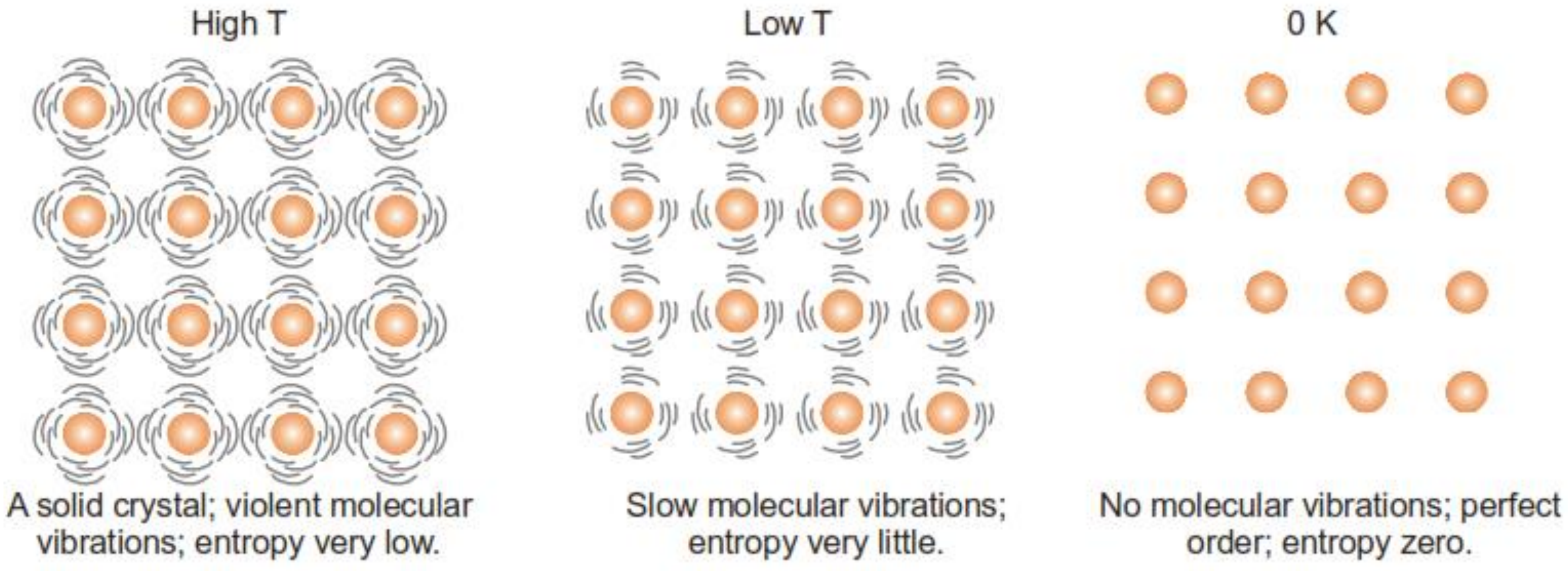
Statement of the Third law

- If we cool the solid crystal still further, the vibration of molecules held in the crystal lattice gets slower and they have very little freedom of movement (very little disorder) and hence very small entropy.
- Finally, at absolute zero all molecular vibration ceases and water molecules are in perfect order.
- Now the entropy of the system will be zero.
- This leads us to the statement of the third law of thermodynamics which states that:

Statement of the Third law

- **“at absolute zero, the entropy of a pure crystal is also zero”.**
- That is,

$$S = 0 \;\; at \;\; T = 0\,K.$$



Numerical definition of entropy

- We have discussed the physical definition of entropy.
- But classical thermodynamics does not require a physical explanation of the concept of entropy.
- All that we need is an operational definition so that we can calculate the entropy change of the system and the surroundings.
- In 1850 Clausius introduced a numerical definition of entropy.

Numerical definition of entropy

- According to him entropy of a system (not undergoing chemical or physical changes), is a constant quantity when there is no communication of heat.
- When heat (*q*) flows into a system, *the entropy increases by*

$$q/T\ .$$

- Heat flowing out of a system produces a corresponding decrease.

Numerical definition of entropy

- Thus entropy could be precisely defined as: ***for a reversible change taking place at a fixed temperature (T), the change in entropy (ΔS) is equal to heat energy absorbed or evolved divided by the temperature (T).***
- That is,

$$\Delta S = \frac{q}{T}$$

Numerical definition of entropy

- If heat is absorbed, then ΔS is positive and there will be increase in entropy.
- If heat is evolved, ΔS is negative and there is a decrease in entropy.
- In the SI system, the units are joules per mole per degree i.e., $J\ mol^{-1}\ K^{-1}$.

Standard entropy

- From the third law, we know that the entropy of a pure crystal is zero at absolute zero (K)
- Therefore, it is possible by measurement and calculation to find the actual amount of entropy that a substance possesses at any temperature above 0 K.
- It is often referred to as **absolute entropy.**
- The absolute entropy of a substance at 25^{o}C (298 K) and one atmosphere pressure is called **the standard entropy;** S^o**.**

Standard entropy

- **The absolute entropy of elements is zero only at 0 K in a perfect crystal, and** standard entropies of all substances at any temperature above 0 K always have positive values.

TABLE 9.1. STANDARD ENTROPIES OF SOME SUBSTANCES (25°C, 1 ATM)

Substance	Entropy, S^o cal mol^{-1} K^{-1}	Entropy, S^o J mol^{-1} K^{-1}	Substance	Entropy, S^o cal mol^{-1} K^{-1}	Entropy, S^o J mol^{-1} K^{-1}
Ag (*s*)	41.32	172.9	$H_2(g)$	31.21	130.6
AgCl (*s*)	58.5	24.5	$H_2O(g)$	45.11	188.7
Al (*s*)	6.77	28.3	$H_2O(l)$	16.72	69.96
Al_2O_3 (*s*)	12.19	51.0	HCl (*g*)	44.62	186.7
C (*s*, graphite)	0.58	2.4	HNO_3 (*l*)	37.19	155.6
CO (*g*)	47.30	197.9	H_2SO_4 (*l*)	37.5	157.0
CO_2 (*g*)	51.06	213.6	Hg (*l*)	18.2	76.1

Standard entropy

- Once we know the entropies of a variety of substances, we can calculate the standard entropy change, ΔS^o, *for chemical reactions.*

$$\Delta S^o = \sum S^o_{(products)} - \sum S^o_{(reactants)}$$

- The entropy of formation of 1 mole of a compound from the elements under standard conditions is called the ***Standard entropy of formation*** and is denoted by $\Delta_f S^o$

Standard entropy

- We can calculate the value of entropy of a given compound from the values of S^o of elements.

$$S^o_f = S^o_{(compound)} - \sum S^o_{(elements)}$$

Standard entropy

SOLVED PROBLEM 1. Urea hydrolyses in the presence of water to produce ammonia and carbon dioxide.

$$CO(NH_2)_2\,(aq) + H_2O\,(l) \longrightarrow CO_2(g) + 2NH_3(g)$$

What is the standard entropy change for this reaction when 1 mole of urea reacts with water ? The standard entropies of reactants and products are listed below :

Substance	S^o(cal/mole K)
$CO(NH_2)_2$	41.55
$H_2O\,(l)$	16.72
$CO_2\,(g)$	51.06
$NH_3\,(g)$	46.01

SOLUTION

We know that

$$\Delta S^{o} = \sum S^{o}\,(\text{products}) - \sum S^{o}\,(\text{reactants})$$

or

$$\Delta S^{o} = \left(S^{o}_{CO_2} + 2S^{o}_{NH_3}\right) - \left(S^{o}_{CO(NH_2)_2} + S^{o}_{H_2O}\right)$$

$$= [51.06 + 2 \times 46.01] - [41.55 + 16.72]\ \text{cal K}^{-1}$$

$$= \mathbf{84.81\ cal\ K^{-1}}$$

SOLVED PROBLEM 2. Calculate the standard entropy of formation, $\Delta S^o{}_f$, of $CO_2(g)$. Given the standard entropies of $CO_2(g)$, $C(s)$, $O_2(g)$, which are 213.6, 5.740, and 205.0 JK^{-1} respectively.

SOLUTION

We know that

$$S^o{}_f = S^o{}_{compound} - \sum S^o{}_{elements}$$

or

$$S^o{}_f = S^o{}_{CO_{2(g)}} - \left[S^o{}_{C_{(s)}} + S^o{}_{O_2(g)}\right]$$

Substituting the values

$$S^o{}_f = 213.6 - [5.740 + 205.0]\ JK^{-1}$$

$$= (213.6 - 210.74)\ JK^{-1} = \mathbf{2.86\ JK^{-1}}$$

Some useful definitions

1) **Cyclic Process**
   - When a system undergoes a series of changes and in the end returns to its original state, it is said to have completed as cycle.
   - The whole process comprising the various changes is termed a **cyclic process.**
   - Since the internal energy of a system depends upon its state, it stands to reason that in cyclic process the net change of energy is zero.

Some useful definitions

1) **Cyclic Process**
   - When a system undergoes a series of changes and in the end returns to its original state, it is said to have completed as cycle.
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Entropy change for an ideal gas

- Entropy is a state function and its value depends on two of three variables *T, P and V.*

a) T and V as Variables

- Let us consider *n moles of an ideal gas occupying volume V at pressure P and temperature T.*
- *If* the system absorbs dq_{rev} heat reversibly then increase in entropy is given by:

Entropy change for an ideal gas

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

- According to the first law of thermodynamics

$$dq_{rev} = dE + PdV$$

- Therefore:

$$dS = \frac{dE + PdV}{T}$$

Entropy change for an ideal gas

- For an ideal gas:

$$PV = nRT$$

- And

$$P = \frac{n}{V}RT$$

- since

$$dE = n\,C_v\,dT$$

Entropy change for an ideal gas

- where C_v is the molar heat at constant volume.
- Substituting this into the entropy equation gives:

$$dS = \frac{n\,C_v\,dT + \left(\frac{n}{V}RT\right)dV}{T}$$

- or

$$dS = n\,C_v\,\frac{dT}{T} + n\,R\,\frac{dV}{V}$$

Entropy change for an ideal gas

- Integrating between the limits S_1, S_2 ; T_1, T_2; and V_1, V_2 we get.

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} n C_v \frac{dT}{T} + \int_{V_1}^{V_2} n R \frac{dV}{V}$$

- *or*

$$\Delta S = S_2 - S_1 = n C_v \ln \frac{T_2}{T_1} + n R \ln \frac{V_2}{V_1}$$

- *Or*

$$\Delta S = 2.303\, n C_v \log \frac{T_2}{T_1} + 2.303\, R \log \frac{V_2}{V_1} \quad (i)$$

Entropy change for an ideal gas

- For 1 mole of an ideal gas

$$\Delta S = 2.303\, C_v \log \frac{T_2}{T_1} + 2.303\ R \log \frac{V_2}{V_1}$$

b) P and T as Variables

- Let P_1 be the pressure in the initial state and P_2 in the final state then

- $$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \textbf{or} \quad \frac{V_2}{V_1} = \frac{P_1 T_2}{P_2 T_1}$$

Entropy change for an ideal gas

- Substituting for V_2/V_1 gives:

$$\Delta S = n\,C_v \ln\frac{T_2}{T_1} + n\,R \ln\frac{P_1\,T_2}{P_2\,T_1}$$

$$= n\,C_v \ln\frac{T_2}{T_1} + n\,R \ln\frac{T_2}{T_1} + n\,R \ln\frac{P_1}{P_2}$$

$$= n\,(C_v + R) \ln\frac{T_2}{T_1} + n\,R \ln\frac{P_1}{P_2}$$

$$= nC_P \ln\frac{T_2}{T_1} + n\,R \ln\frac{P_1}{P_2} \qquad [\because C_P = C_v + R]$$

Entropy change for an ideal gas

- Or

$$\Delta S = 2.303 \times n \times C_p \log \frac{T_2}{T_1} + 2.303 \times n \times R \log P_1/P_2 \quad (ii)$$

- Lets look at some specific conditions
- **Case 1. At constant temperature for an isothermal process**
- In this case $T_1 = T_2$, the equation *(i) and (ii) reduce to*

Entropy change for an ideal gas

$$\Delta S_T = 2.303 \times n \times R \log \frac{V_2}{V_1}$$

- And

$$\Delta S_T = 2.303 \times n \times R \log \frac{P_1}{P_2}$$

- In an isothermal expansion $V_2 > V_1$ or $P_1 > P_2$ hence ΔS_T is positive whereas in isothermal contraction $V_2 < V_1$ or $P_1 < P_2$, ΔS_T is negative.

Entropy change for an ideal gas

- **Case 2: At constant pressure (Isobaric process)**
- In this case $P_1 = P_2$, the equation (*ii)* reduces to:

$$\Delta S_P = 2.303\, n\, C_P \log \frac{T_2}{T_1}$$

- **Case 3: At constant volume for an isobaric process**
- In this case $V_1 = V_2$, the equation (*i) reduces to*

$$\Delta S_v = 2.303 \times n \times C_v \log \frac{T_2}{T_1}$$

SOLVED PROBLEM 1

- Calculate the entropy change involved in thermodynamic expansion of 2 moles of a gas from a volume of 5 litres to a volume of 50 litres at 303 K.
- **Solution**. Here $n = 2$; $V_1 = 5$ litres; $V_2 = 50$ litres

using the relation $\Delta S_T = 2.303 \times n \times R \log \frac{V_2}{V_1}$

on substituting the values we get

$$\Delta S_T = 2.303 \times 2 \times 8.314 \times \log \frac{50}{5}$$

$$= \mathbf{38.29\ JK^{-1}}$$

SOLVED PROBLEM 2

SOLVED PROBLEM 2. Calculate the entropy change when 2 moles of an ideal gas are allowed to expand isothermally at 293 K from a pressure of 10 atmosphere to a pressure of 2 atmosphere.

SOLUTION. We know

$$\Delta S_T = 2.303 \times n \times R \times \log \frac{P_1}{P_2}$$

Here $n = 2;\ R = 8.314\ \text{J}$

$P_1 = 10\ \text{atm};\ P_2 = 2\ \text{atm.}$

Substituting the values we get

$$\Delta S_T = 2.303 \times 2 \times 8.314 \times \log \frac{10}{2}$$

$$= 2.303 \times 2 \times 8.314 \times 0.6990$$

$$= \mathbf{26.76\ JK^{-1}}$$