



Walther Nernst

Nernst suggested that the change in entropy for chemical reactions approached 0 as the temperature approached 0 K.

$$\Delta_r S \rightarrow 0 \quad \text{as} \quad T \rightarrow 0$$



Max Planck

I think that the entropy of a pure substance approaches 0 at 0 K!

The Third Law: Every substance has a finite positive entropy, but at 0 K the entropy may become 0, and does so in the case of a perfectly crystalline substance.

The third law was formulated *before* the full development of quantum theory. However, statistical thermodynamics gives us *molecular insight* to the third law.

$$S = k_B \ln W$$

At 0 K, we expect that the system will be in its lowest energy state and therefore $W = 1$, $S = 0$.

$$S = -k_B \sum_j p_j \ln p_j \quad p_0 = 1 \text{ and all other } p_j\text{'s} = 0. \quad S = 0.$$



The 1st and 2nd Law of Thermodynamics introduced new state functions. The 3rd Law of Thermodynamics simply provides an absolute scale for entropy.

Law 1

$$dU =$$

$$\delta q_{rev} =$$

← Law 2

$$dU = TdS - PdV$$

1st and 2nd Law

$$dH = d(U + PV) =$$

$$dH = TdS + VdP$$

1st and 2nd Law

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \qquad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[P + \left(\frac{\partial U}{\partial V}\right)_T \right] \qquad \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T} \left[\left(\frac{\partial H}{\partial P}\right)_T - V \right]$$

We work at constant pressure most of the time...

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \quad \xrightarrow{\text{Integrate with respect to } T \text{ at constant } P}$$

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_P(T)}{T} dT$$

If $T_1 = 0 \text{ K}$

$$\Delta S = S(T_2) = \int_0^{T_2} \frac{C_P(T)}{T} dT$$



$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_P(T)}{T} dT \quad \text{If we know } C_p(T) \text{ we can find } \Delta S$$

What happens at phase transitions?

$$\Delta_{trs} S = \frac{q_{rev}}{T_{trs}} \quad \text{At constant P:} \quad \Delta_{trs} S = \frac{\Delta_{trs} H}{T_{trs}}$$

$$S(T') = \int_0^{T_{fus}} \frac{C_p^s(T)}{T} dT + \frac{\Delta_{fus} H}{T_{fus}} + \int_{T_{fus}}^{T_{vap}} \frac{C_p^l(T)}{T} dT + \frac{\Delta_{vap} H}{T_{vap}} + \int_{T_{vap}}^{T'} \frac{C_p^g(T)}{T} dT$$

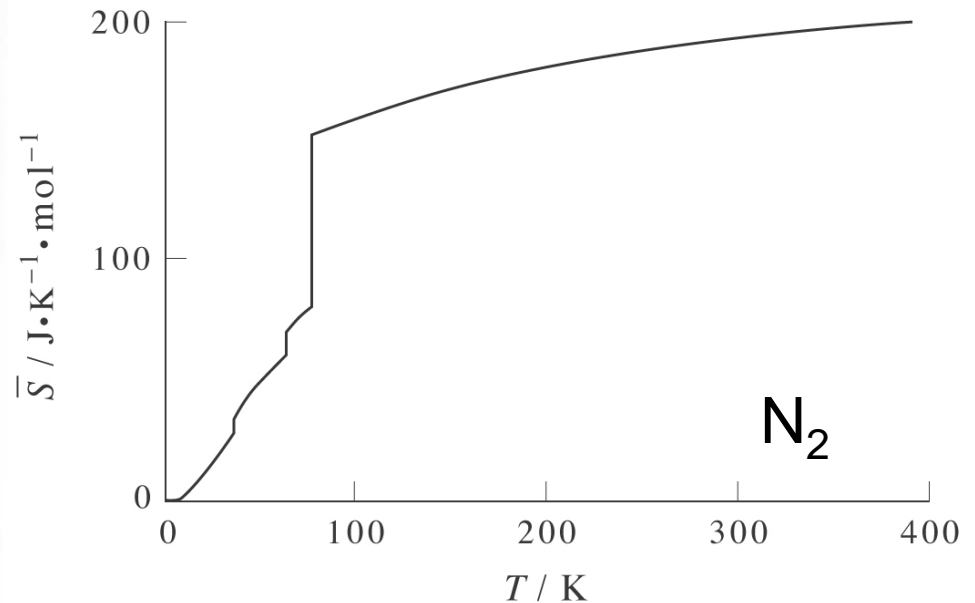


TABLE 7.1 Table 21.1
The standard molar entropy of nitrogen at 298.15 K.

Process	$\bar{S} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
0 to 10.00 K	2.05
10.00 to 35.61 K	25.79
Transition	6.43
35.61 to 63.15 K	23.41
Fusion	11.2
63.15 to 77.36 K	11.46
Vaporization	72.0
77.36 K to 298.15 K	39.25
Correction for nonideality	<u>0.02</u>
Total	191.6

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Figure 21.1



Values of entropies for gases given in the literature are standard entropies. These are by convention corrected for the non-ideality of gases (to be discussed in detail in Ch 22).





Peter Debye

$$C_P^s(T) \rightarrow T^3$$

as $T \rightarrow 0$

Less than 15 K



$$\bar{C}_P = \frac{12\pi^4}{5} R \left(\frac{T}{\Theta_D} \right)^3$$

$$0 < T \leq T_{low}$$

$$\bar{S}(T) = \frac{12\pi^4 R}{5\Theta_D^3} \int_0^{T'} T^2 dT = \frac{\bar{C}_P(T)}{3}$$



Remember:

$$S = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

$$S = k_B \ln \sum_j e^{-E_j/k_B T} + \frac{1}{T} \frac{\sum_j E_j e^{-E_j/k_B T}}{\sum_j e^{-E_j/k_B T}}$$

How does S behave as the temperature goes to 0?

Is this consistent with the 3rd Law of Thermodynamics?



TABLE 7.2 Table 21.2

Standard molar entropies (S°) of various substances at 298.15 K.

Substance	$S^\circ/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	Substance	$S^\circ/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Ag(s)	42.55	HCl(g)	186.9
Ar(g)	154.8	HCN(g)	201.8
Br ₂ (g)	245.5	HI(g)	206.6
Br ₂ (l)	152.2	H ₂ O(g)	188.8
C(s)(diamond)	2.38	H ₂ O(l)	70.0
C(s)(graphite)	5.74	Hg(l)	75.9
CH ₄ (g)	186.3	I ₂ (s)	116.1
C ₂ H ₂ (g)	200.9	I ₂ (g)	260.7
C ₂ H ₄ (g)	219.6	K(s)	64.7
C ₂ H ₆ (g)	229.6	N ₂ (g)	191.6
CH ₃ OH(l)	126.8	Na(s)	51.3
CH ₃ Cl(g)	234.6	NH ₃ (g)	192.8
CO(g)	197.7	NO(g)	210.8
CO ₂ (g)	213.8	NO ₂ (g)	240.1
Cl ₂ (g)	223.1	O ₂ (g)	205.2
H ₂ (g)	130.7	O ₃ (g)	238.9
HBr(g)	198.7	SO ₂ (g)	248.2

TABLE 7.3 Table 21.3

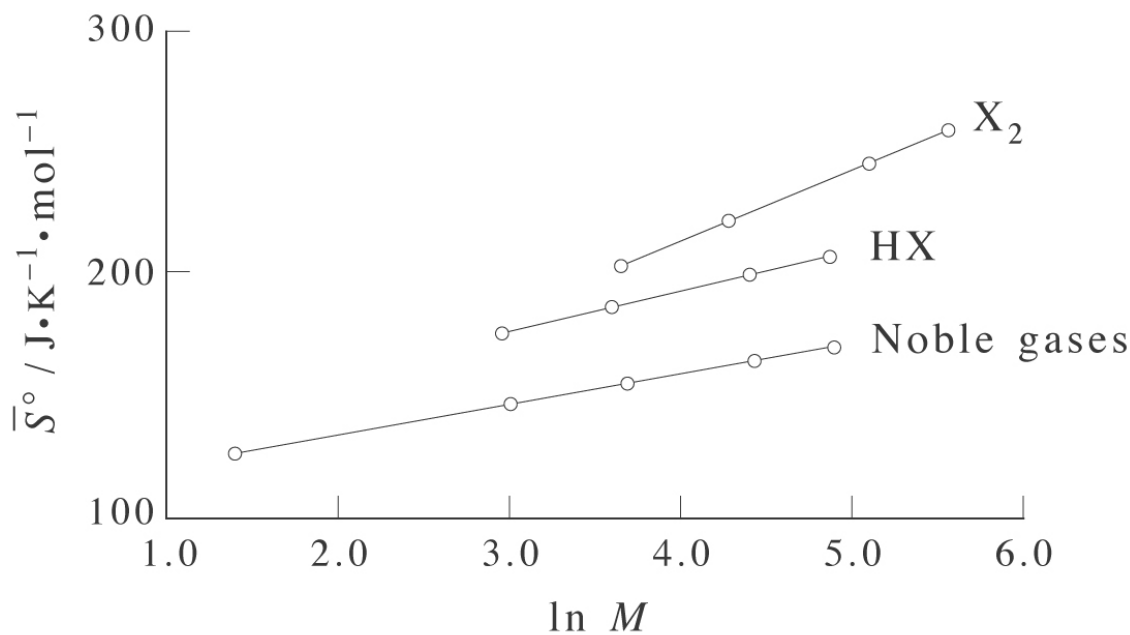
Standard molar entropies (S°) for the noble gases, the gaseous halogens, and the hydrogen halides at 298.15 K.

Noble gas	$S^\circ/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	Halogen	$S^\circ/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	Hydrogen halide	$S^\circ/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
He(g)	126.2	F ₂ (g)	202.8	HF(g)	173.8
Ne(g)	146.3	Cl ₂ (g)	223.1	HCl(g)	186.9
Ar(g)	154.8	Br ₂ (g)	245.5	HBr(g)	198.7
Kr(g)	164.1	I ₂ (g)	260.7	HI(g)	206.6
Xe(g)	169.7				

What are the trends for:
Phase: Gas, liquid, solid
Mass
of atoms

Tables are often a combination of statistical thermodynamics and calorimetric values.

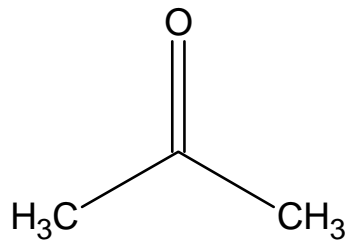




Function of Mass

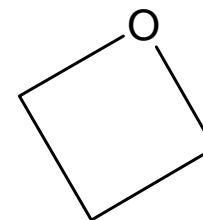
From what E term?

Acetone



298 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

Trimethylene oxide

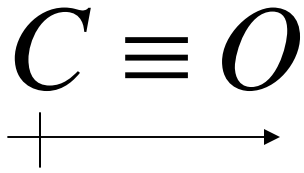


274 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

$\text{C}_3\text{H}_6\text{O}$

Why?





At 81.6 K:

$$\bar{S}_{calc} = 160.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\bar{S}_{exp} = 155.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\bar{S}_{calc} > \bar{S}_{exp}$$

CO has a very small dipole moment so the molecules do not have a strong tendency to line up in an energetically favorable way. As a result, in the crystal (i.e., low T form) gets “locked” into its own orientation and cannot find the state of lowest energy (i.e., where $W = 1$).

$$S_{residual} = \bar{S}_{calc} - \bar{S}_{exp}$$

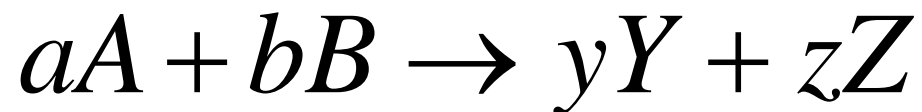
$$W = 2^N \quad S = k_B \ln W$$

$$S_{residual} = k_B \ln 2^N = Nk_B \ln 2$$

$$\bar{S} = R \ln 2 = 5.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\bar{S}_{calc} = \bar{S}_{res} + \bar{S}_{exp} = 161.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

As used in Homework #3...



$$\Delta_r S^\circ = yS^\circ[Y] + zS^\circ[Z] - aS^\circ[A] - bS^\circ[B]$$

