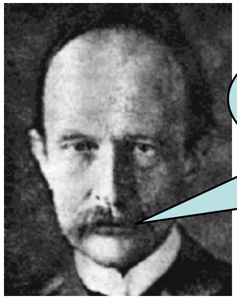
The Third Law of Thermodynamics

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

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.

Statistical Mechanics and the 3rd Law

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 $W = 1$, $S = 0$.

$$S = -k_B \sum_j p_j \ln p_j$$

$p_0 = 1$ and all other p_j's $= 0$. S = 0.

1st and 2nd Law vs 3rd Law

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

Law 2

$$\delta q_{rev} = TdS$$

Law 1

$$dU = \delta w_{rev} + \delta q_{rev}$$

$$-PdV$$

$$dU = TdS - PdV$$

1st and 2nd Law

$$dH = d(U + PV) = dU + PdV + VdP$$

$$dH = TdS + VdP$$

1st and 2nd Law

Results of EX-TL1

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

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

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

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

We work at constant pressure most of the time…

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

Integrate with respect to T 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 K

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

Phase Transitions!!

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

If we know $Cp(T)$ we can find ΔS

What happens at phase transitions?

$$\Delta_{trs} S = \frac{q_{rev}}{T_{trs}}$$

At constant P:

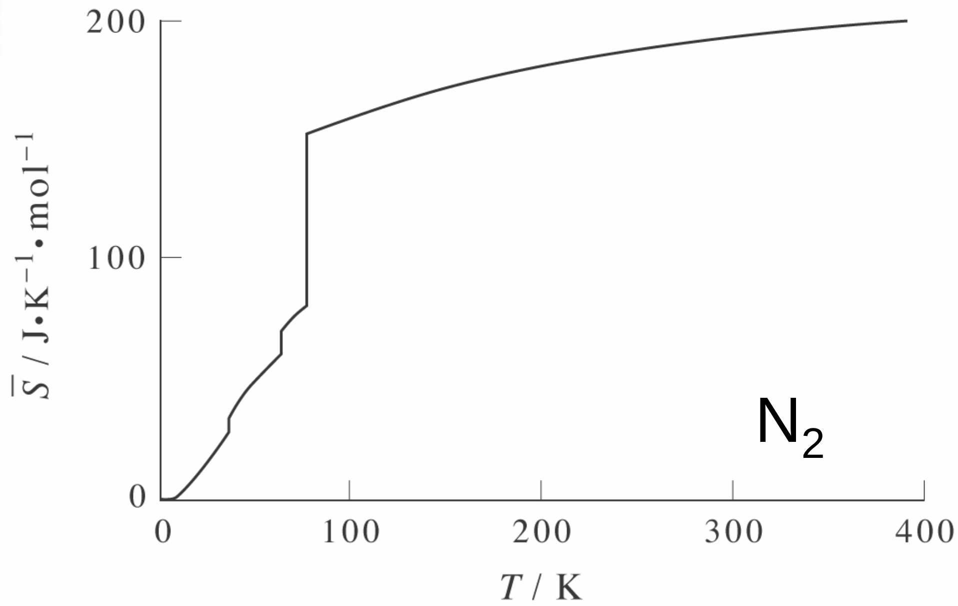
$$\Delta_{trs} S = \frac{\Delta_{trs} H}{T_{trs}}$$

Practical Absolute Entropies

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

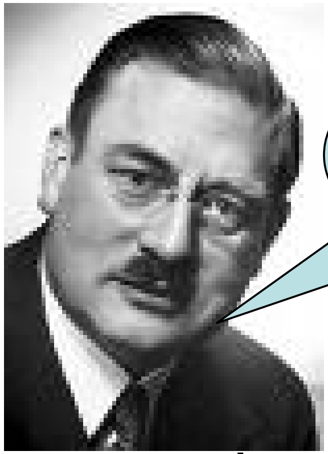
Process	$\overline{S}$/J·K^{-1}·mol^{-1}
0 to 10.00 K	2.05
10.00 to 35.61 K	25.79
Transition	6.43
35.61 to 63.15 K	23.41
Fusion	11.2
63.15 to 77.36 K	11.46
Vaporization	72.0
77.36 K to 298.15 K	39.25
Correction for nonideality	0.02
Total	191.6

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).

Low T and Debye Theory



Peter Debye

$$C_P^s(T) \rightarrow T^3$$
as $T \rightarrow 0$

Less than 15 K

$$\overline{C}_P = \frac{12\pi^4}{5} R \left(\frac{T}{\Theta_D} \right)^3 \qquad 0 < T \leq T_{low}$$

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

Partition Functions and 3rd Law

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?

See page 861-862 for proofs. 862 and 863 also discusses diatomic and polyatomics.

Literature Values and Trends

TABLE 7.2 Table 21.2

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

Substance	S°/J·K^{-1}·mol^{-1}	Substance	S°/J·K^{-1}·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_2O(g)	188.8
C(s)(diamond)	2.38	H_2O(l)	70.0
C(s)(graphite)	5.74	Hg(l)	75.9
CH_4(g)	186.3	I_2(s)	116.1
C_2H_2(g)	200.9	I_2(g)	260.7
C_2H_4(g)	219.6	K(s)	64.7
C_2H_6(g)	229.6	N_2(g)	191.6
CH_3OH(l)	126.8	Na(s)	51.3
CH_3Cl(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

What are the trends for:

Phase: Gas, liquid, solid

Mass

of atoms

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

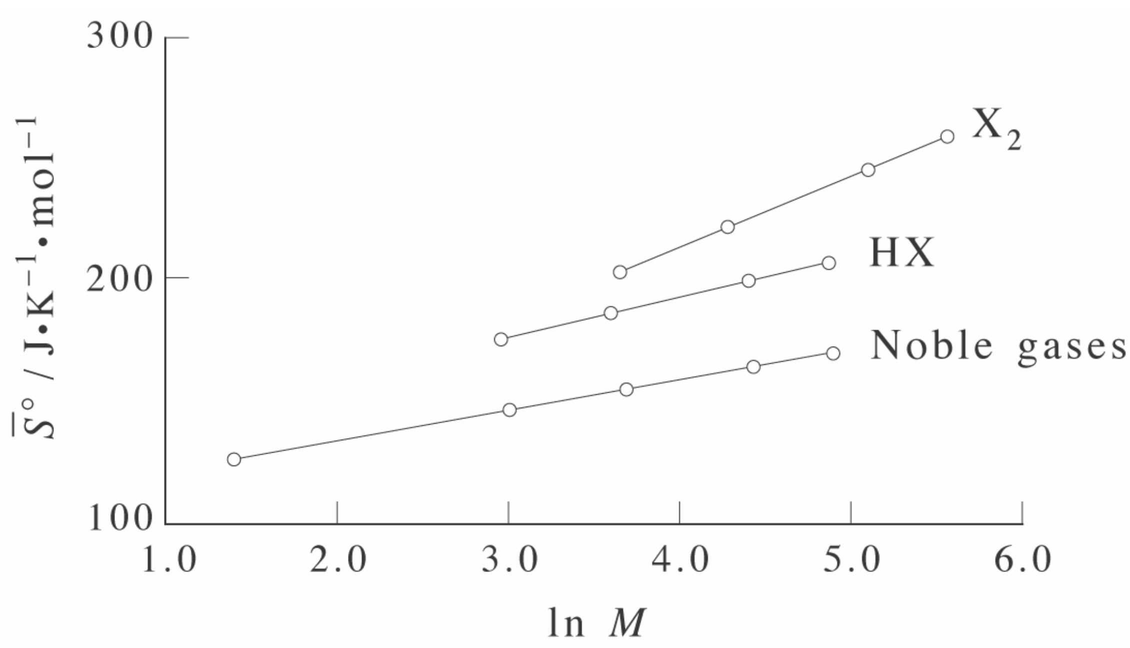
TABLE 7.3 Table 21.3

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

Noble gas	S°/J·K^{-1}·mol^{-1}	Halogen	S°/J·K^{-1}·mol^{-1}	Hydrogen halide	S°/J·K^{-1}·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				

Entropy and Molecular Structure

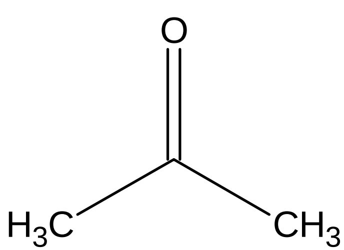
TL-10



Function of Mass

From what E term?

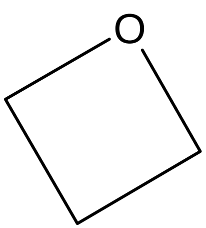
Acetone



298 J·K^{-1}·mol^{-1}

C_3H_6O

Trimethylene oxide

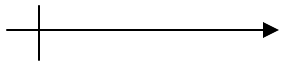


274 J·K^{-1}·mol^{-1}

Why?

Sometimes there is not agreement

$$C \equiv O$$



At 81.6 K:

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

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

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

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).

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

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

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

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

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

Entropy changes of chemical reactions

As used in Homework #3…

$$aA + bB \rightarrow yY + zZ$$

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