Statistical Molecular Thermodynamics

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Video 7.5

Third Law Entropies

298 K Standard Molar Entropies

units of $J \bullet K^{-1} \bullet mol^{-1}$

Solids

Carbon (diamond)	2.4	*The stiffer lattice of diamond compared to graphite leads to lower entropy*
Carbon (graphite)	5.7	
Sodium	51.3	*Insulators have substantially lower entropies than conductors as the latter have many states accessible to conduction electrons*
Potassium	64.7	
Silver	42.6	

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units of $J \bullet K^{-1} \bullet mol^{-1}$

Liquids vs Gases

	Liquid	Gas
Water	70.0	188.8
Bromine	152.2	245.5

The condensed nature of the liquid reduces entropy compared to the gas; the greater mass of Br_2 compared to H_2O leads to greater entropy but in the gas phase this is somewhat balanced by an additional rotational degree of freedom for the non-linear water molecules.

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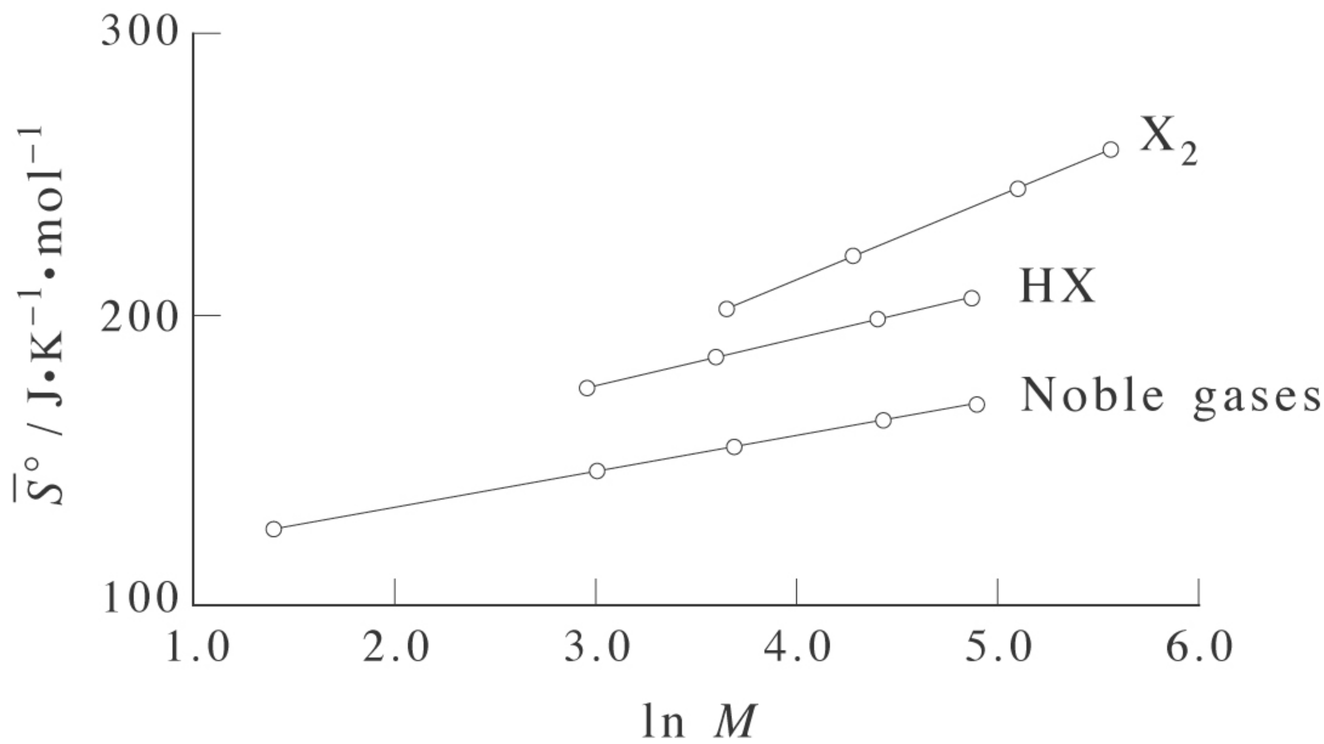
units of J•K^{-1}•mol^{-1}

Gases

He	126.2			HF	173.8
Ne	146.3	F_2	202.8 ↔	HCl	186.9
Ar	154.8	Cl_2	223.1 ↔	HBr	198.7
Kr	164.1	Br_2	245.5 ↔	HI	206.6
Xe	169.7	I_2	260.7		

$S_{\mathrm{trans}} = f(M)$ $\quad S_{\mathrm{rot}} = f(\Theta_{\mathrm{rot}})$ $\quad [S_{\mathrm{vib}} = f(\Theta_{\mathrm{vib}})]$

298 K Standard Molar Entropies



Variation within a series primarily dictated by mass, but relationships between *series differentiated by rotational entropy.*

298 K Standard Molar Entropies

units of $J \cdot K^{-1} \cdot mol^{-1}$

near quantitative agreement between measured values and those computed from the partition function for an ideal gas

Polyatomic gases

	calc	expt
CO_2	213.8	213.7
NO_2	240.1	240.2
CH_4	186.3	186.3
C_2H_2	200.9	200.8
C_2H_4	219.6	219.6
C_2H_6	229.6	229.5

linear vs non-linear (CO_2, NO_2)

Increasing mass and rotational moments of inertia (CH_4, C_2H_2, C_2H_4, C_2H_6)

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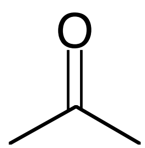
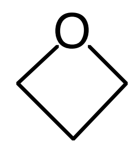
units of J•K^{-1}•mol^{-1}

Polyatomic gases



C_3H_6O



acetone

trimethylene oxide

298 J•K^{-1}•mol^{-1}

274 J•K^{-1}•mol^{-1}

Less entropy when the bonds are constrained in a strained ring.

Residual Entropy

$C\equiv O$

carbon monoxide

at 81.6 K (boiling point):

$$\overline{S}_{calc} = 160.3\ \mathrm{J \bullet K^{-1} \bullet mol^{-1}}$$

$$\overline{S}_{\exp} = 155.6\ \mathrm{J \bullet K^{-1} \bullet mol^{-1}}$$

residual entropy: $\overline{S}_{calc} - \overline{S}_{\exp}$

CO has a very small dipole moment so the molecules *do not* have a tendency to align in the most energetically favorable way in the ~ 0 K solid. Instead, each CO molecule settles into its own orientation (dipole up or dipole down) and the state of lowest entropy (i.e., $W = 1$) is not reached (the energy required to “spontaneously” flip a molecule is not available at ~ 0 K so the dipoles are “trapped”)

$$\overline{W} = 2^{N_A}\left(\approx \Omega\right)$$

$$\overline{S} = k_{\mathrm{B}} \ln \overline{W} = k_{\mathrm{B}} \ln 2^{N_A} = R \ln 2$$

$$\overline{S}(0) = R \ln 2 = 5.7\ \mathrm{J \bullet K^{-1} \bullet mol^{-1}}$$

$$5.7 + 155.6 = 161.3\ \mathrm{J \bullet K^{-1} \bullet mol^{-1}}$$