

## 21.8: Spectroscopic Entropies sometimes disagree with Calorimetric Entropies

The entropy of gases can be experimentally measured using calorimetry ( $S_{\text{exp}}^{\circ}$ ) or calculated using spectroscopic methods ( $S_{\text{calc}}^{\circ}$ ). For most molecules, the experiment and calculated values are in a good agreement, however, this is not true for all molecules. The discrepancy is referred to as residual entropy:

$$\bar{S}_{\text{calc}} - \bar{S}_{\text{exp}}$$

Residual entropy arises from a material that can have many different states at 0 K. The third law of thermodynamics states that at zero kelvin, a substance will have an entropy of zero. In substances, such as glass, ice, and carbon monoxide, the substance can exist in many different configurations; it is not a perfect crystal, but must still have zero entropy according to third law. The material has residual entropy.

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