

Chemistry 433

Lecture 12 The Third Law

NC State University

The Third Law of Thermodynamics

The third law of thermodynamics states that every substance has a positive entropy, but at zero Kelvin the entropy is zero for a perfectly crystalline substance. The third law introduces a numerical scale for the entropy. Stated succinctly:

$S(0) = 0$ for all perfectly ordered crystalline materials.

It is commonly said that all motion ceases at absolute zero. Certainly all translation and rotation have ceased at absolute zero. However, the nuclei still vibrate about their equilibrium positions in so-called zero point motion. However, all molecules are in their lowest vibrational state and entropy is zero in any case provided there are no imperfections in the crystal.

Residual Entropy

The first statistical picture of entropy was that of Boltzmann. The function W that represents the number of ways we can distribute N particles into a number of states. Using the function W the entropy can be expressed as:

$$S = k_B \ln W$$

At zero Kelvin the system is in its lowest energy state. For a perfect crystal there is only one way to distribute the energy and $W = 1$, therefore $S = 0$.

However, the entropy not equal to zero at $T = 0$ K if the substance is not a perfect crystal. Although the residual entropy in such cases is a small correction to the entropy calculated for chemical reactions it still leads to an important concept.

CO: an Imperfect Crystal

The molecule CO has a very small dipole moment and there is a finite chance that CO will crystallize as CO:CO:CO instead of CO:OC:CO. For each CO molecule there are two possible orientations of the molecule, therefore there are two ways each CO can exist in the lattice.

The number of ways per molecule is $w = 2$ for each CO.

If we have N CO molecules there are w^N ways or 2^N ways that all of the CO can be distributed. Therefore, the entropy at zero Kelvin is

$$S = k \ln W = k \ln(w^N) = Nk \ln w = nR \ln 2.$$

The entropy at zero Kelvin is known as residual entropy.

There are number of substances that show similar statistical variations in orientation that lead to a residual entropy.

Question

Suppose there are four ways the the molecule CFCIBrI can be oriented in a crystal lattice at zero Kelvin. What is the molar residual entropy?

- A. $4R \ln(2)$
- B. $2R \ln(4)$
- C. $R \ln(2)$
- D. $R \ln(4)$

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Which phrase best summarizes residual entropy?

- A. the entropy of imperfect crystals
- B. the entropy of the lowest energy state
- C. the entropy of rotation
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The Temperature Dependence of Entropy

We have seen calculations for the entropy change for processes. However, it is also possible to calculate the absolute entropy. We can begin with the definition $dS = dq_{\text{rev}}/T$. The heat transferred during a process at constant volume is $dq_{v,\text{rev}} = C_v dT$. Thus, the entropy change at constant volume is:

$$\Delta S = S(T) - S(0) = \int_0^T \frac{C_v(T) dT}{T}$$

We have kept the equation general by showing $C_v(T)$ as a function of temperature. This calculation of the entropy is valid only at constant V . At constant P we find an analogous expression. Starting with the heat transferred, $dq_{p,\text{rev}} = C_p dT$. We have

$$\Delta S = S(T) - S(0) = \int_0^T \frac{C_p(T) dT}{T}$$

The temperature dependence of the heat capacity

The third law of thermodynamics shows that

$$C_p \rightarrow 0 \text{ as } T \rightarrow 0 \text{ K.}$$

It is necessary to treat $C_p(T)$ as a function of temperature for this reason alone. The Einstein and Debye theories of heat capacity can be used to determine the functional form of the heat capacity of at these low temperatures. The Debye law states that the heat capacity depends on T^3 near $T = 0$ K.

At temperatures close to $T = 0$, $C_{V,m} = aT^3$

The constant a is an empirical constant. For practical calculation of the entropy experimental values can be used and the integrals are evaluated numerically.

Question

If there is no residual entropy then at $T = 0$ K we can state that:

- A. $S > 0$ and $C_p > 0$
- B. $S = 0$ and $C_p > 0$
- C. $S > 0$ and $C_p = 0$
- D. $S = 0$ and $C_p = 0$

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Question

Consider the statement $C_p \longrightarrow 0$ as $T \longrightarrow 0$. Which consequence is valid.

- A. It is harder to heat matter near absolute zero, that is it requires more energy per degree of temperature rise.
- B. It is easier to heat matter near absolute zero, that is it requires less energy per degree of temperature rise.
- C. It gets easier to reach absolute zero because it is easier to cool matter at lower temperature.
- D. Both B and C are correct.

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Absolute Entropy

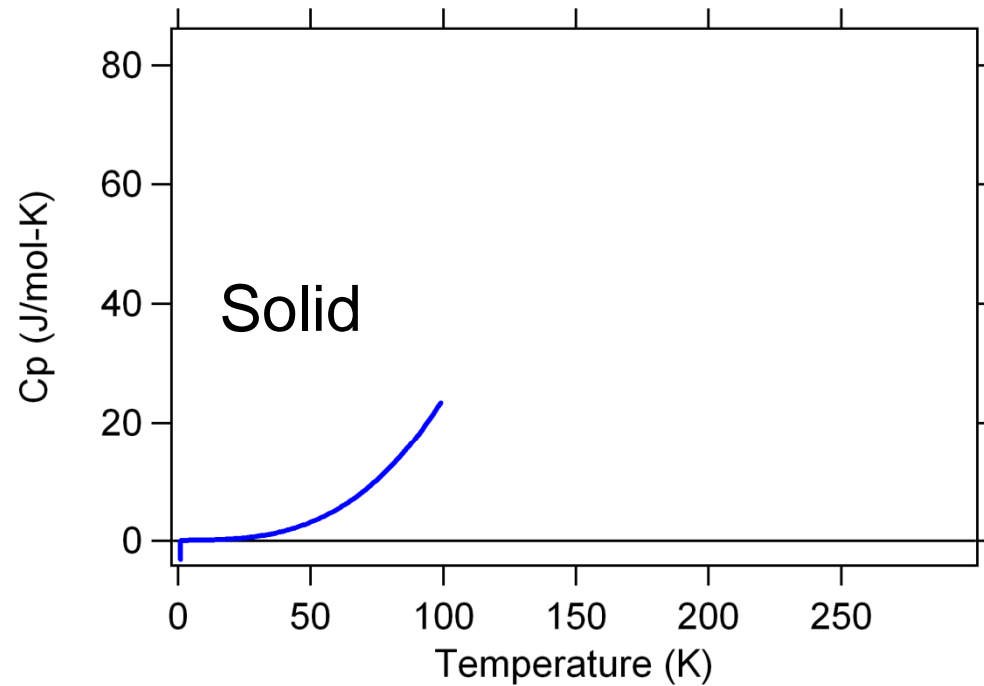
The absolute entropy can be calculated from 0 to any temperature T using the integral of the function $C_p(T)/T$.

If there is a phase transition between 0 and temperature T we can also calculate the contribution to the entropy from the transition.

$$S(T) = \int_0^{T_{fus}} \frac{C_p(T)dT}{T} + \frac{\Delta_{fus}H}{T_{fus}} + \int_{T_{fus}}^{T_{vap}} \frac{C_p(T)dT}{T} + \frac{\Delta_{vap}H}{T_{vap}} + \int_{T_{vap}}^T \frac{C_p(T)dT}{T}$$

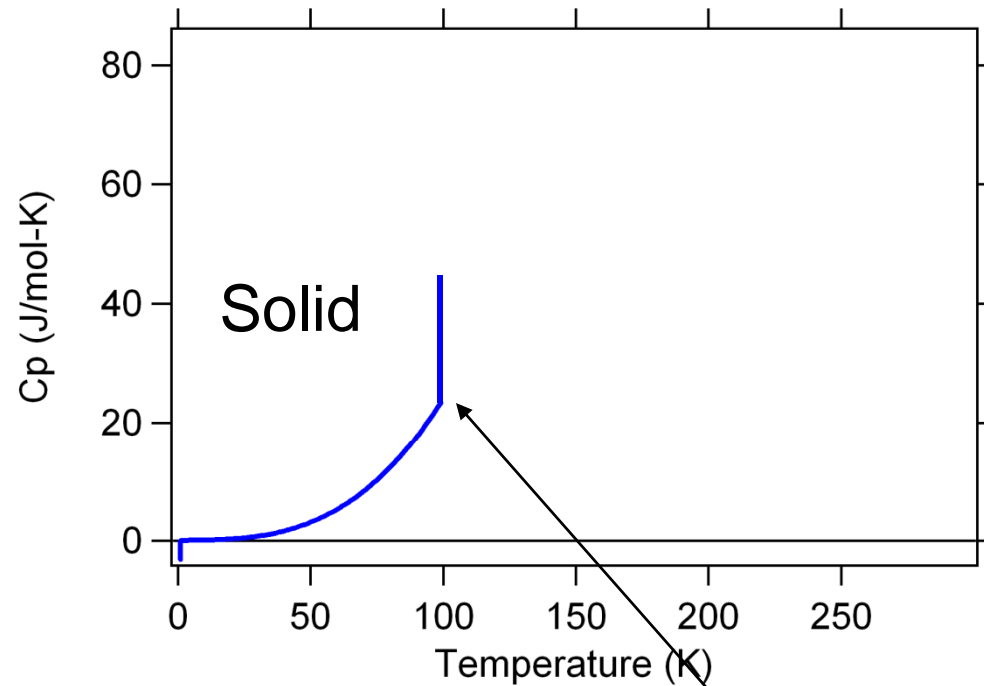
The heat capacity of each phase is different and the heat capacities are also a function of temperature. Remember that the heat capacity approaches zero and the temperature goes to zero so that the C_p is a strong function of T at very low temperature.

Graphical representation



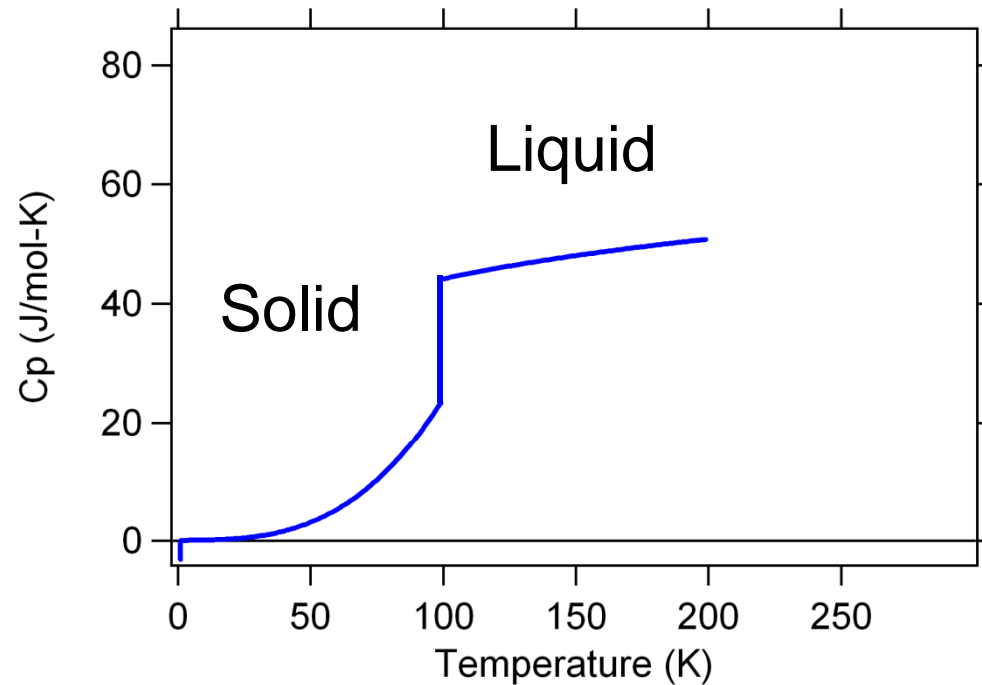
$$S(T) = \int_0^{T_{fus}} \frac{C_p(T) dT}{T}$$

Graphical representation



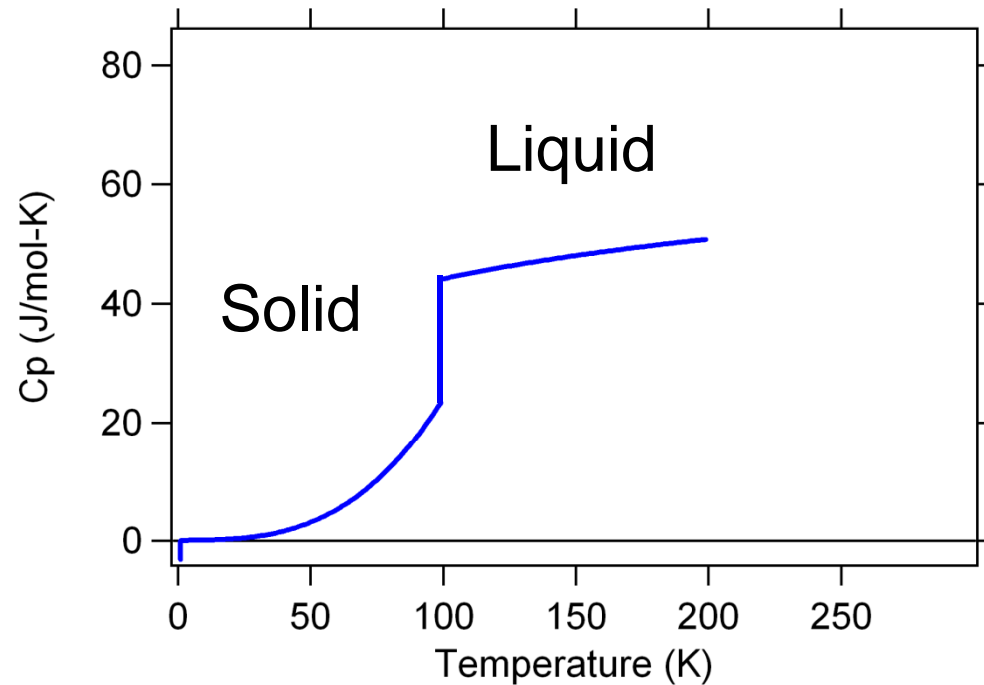
$$S(T) = \int_0^{T_{fus}} \frac{C_p(T)dT}{T} + \frac{\Delta_{fus}H}{T_{fus}}$$

Graphical representation



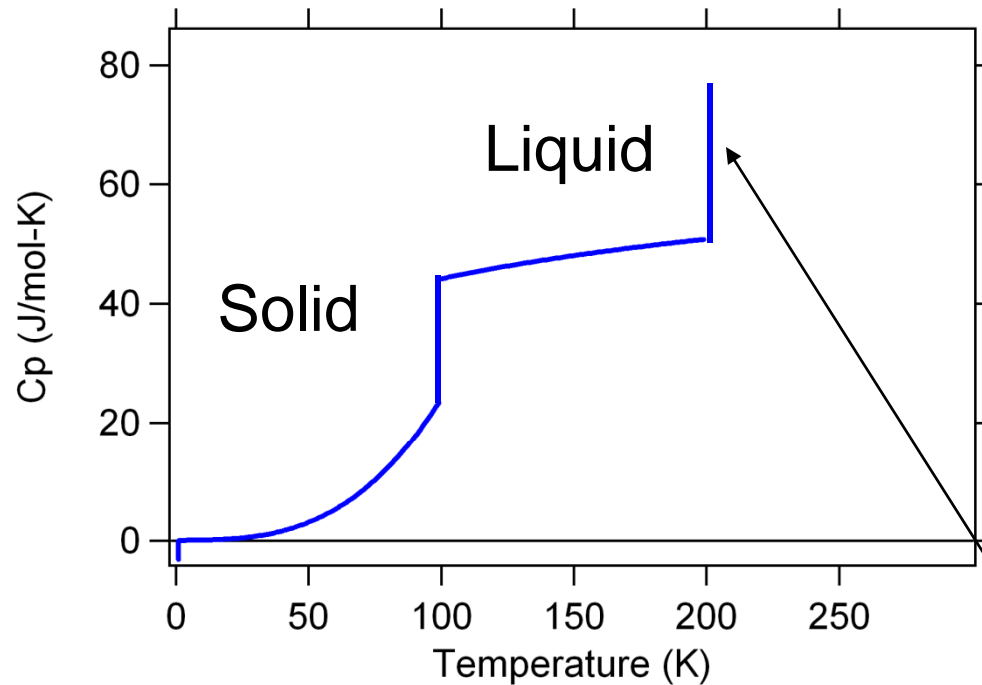
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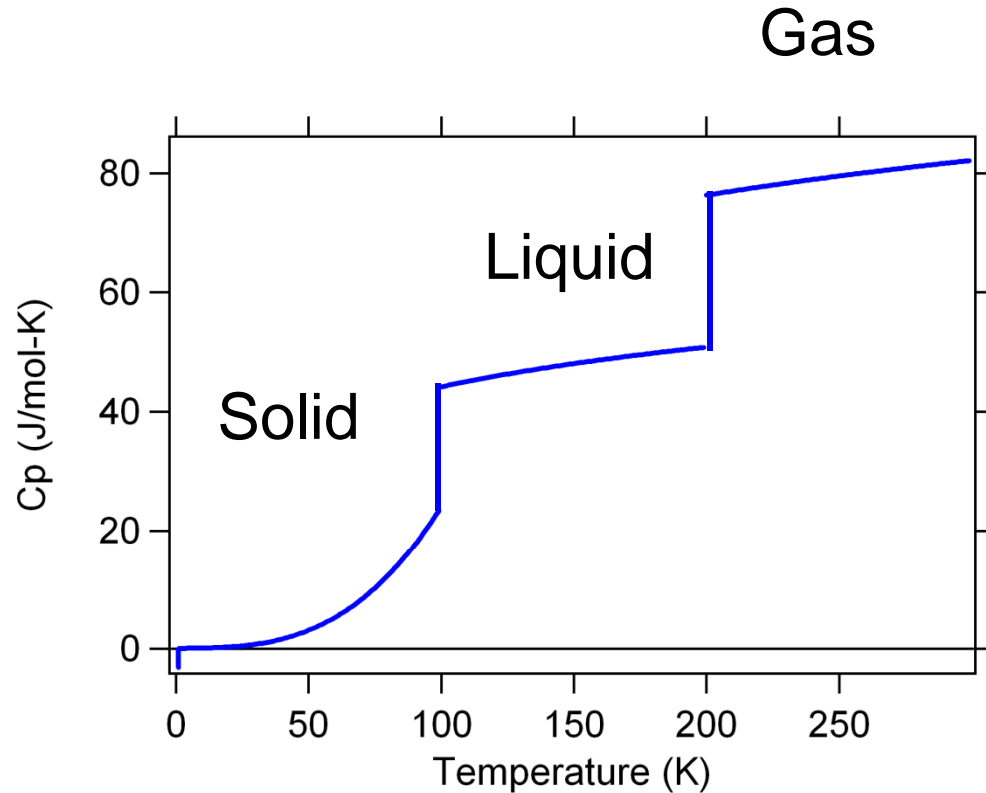
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Graphical representation



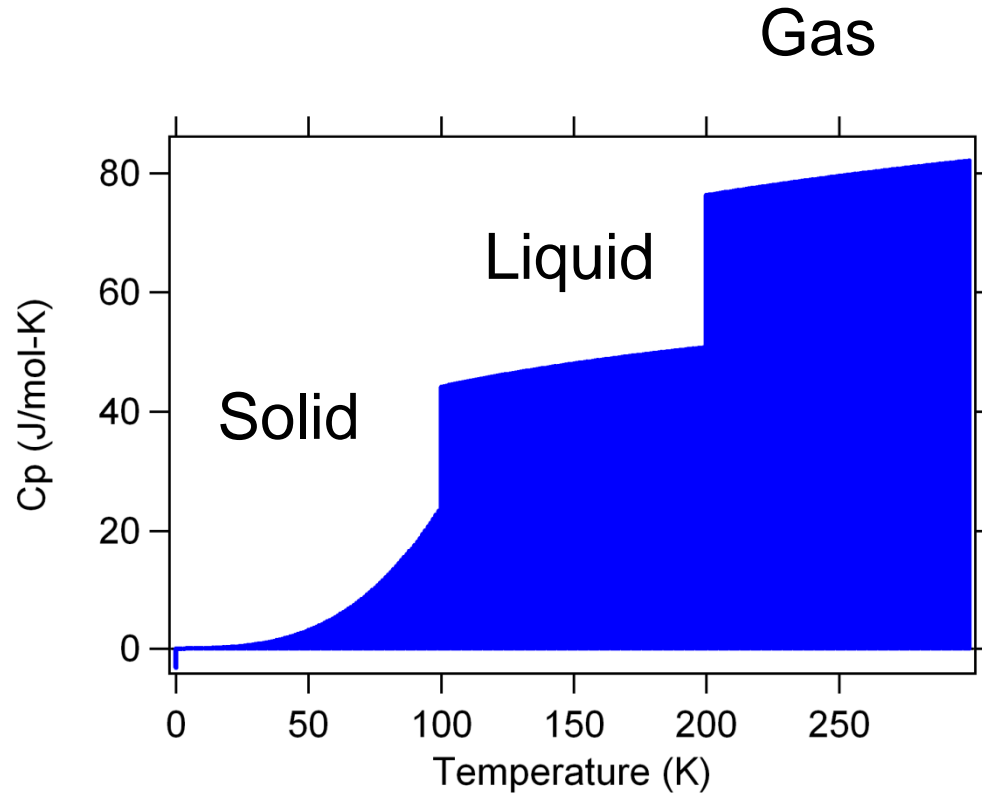
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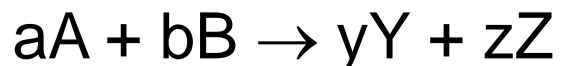
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Absolute Entropies can be used to calculate Reaction Entropies

Entropies are tabulated in order to facilitate the calculation of the entropy change of chemical reactions. For the general reaction



the standard entropy change is given by

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

where the absolute entropies S° are molar quantities.

Note the significant difference compared to enthalpy. There is no such thing as an absolute enthalpy. Instead, we used a reference of the elements in their standard states. In that case the enthalpy of formation was set arbitrarily to zero. Since entropies are zero and $T = 0$ K we can use S° as an absolute quantity.

The standard reaction entropy

The standard reaction entropy, $\Delta_r S^\ominus$, is the difference between the standard molar entropies of the reactants and products, with each term weighted by the stoichiometric coefficient.

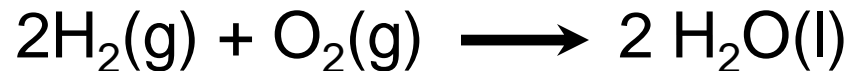
$$\Delta_r S^\ominus = \sum \nu S_m^\ominus(\text{products}) - \sum \nu S_m^\ominus(\text{reactants})$$

The standard state is for reactants and products at 1 bar of pressure. The unit of energy used is J/mol-K.

IMPORTANT: Do not confuse entropy and enthalpy. One common mistake is to set the entropies of elements equal to zero as one does for enthalpies of formation. Elements have an entropy that is not zero (unless the temperature is $T = 0$ K).

An example: formation of H₂O

We apply the absolute entropies of H₂, O₂ and H₂O to the calculation of the entropy of reaction for:



The entropy change is:

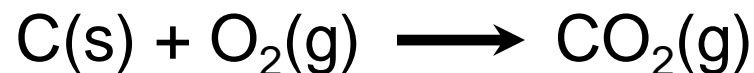
$$\begin{aligned}\Delta S^\ominus &= 2 S^\ominus(\text{H}_2\text{O}, \text{l}) - S^\ominus(\text{O}_2, \text{g}) - 2S^\ominus(\text{H}_2, \text{g}) \\ &= 2(70) - 2(131) - 205 \text{ J/mol-K} \\ &= - 327 \text{ J/mol-K}\end{aligned}$$

This result is not surprising when you consider that 3 moles of gas are being consumed. A gas has a greater number of translational degrees of freedom than a liquid.

On the other hand, it is difficult (at first) to understand how a spontaneous reaction can have such a large negative entropy.

Question

Consider the formation of CO₂.

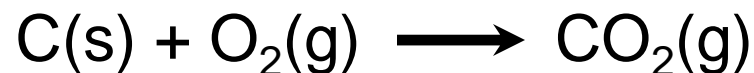


Which is correct?

- A. $\Delta S^\ominus = 0$ (equilibrium)
- B. $\Delta S^\ominus = \Delta H/T$ (phase transition)
- C. $\Delta S^\ominus = S(\text{CO}_2, \text{g}) - S(\text{O}_2, \text{g})$ ($S = 0$ for solids)
- D. $\Delta S^\ominus = S(\text{CO}_2, \text{g}) - S(\text{O}_2, \text{g}) - S(\text{C}, \text{s})$ (reaction)

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The spontaneity of chemical reactions

The spontaneity of chemical reactions must be understood by consideration of both the system and the surroundings. This is one of the most subtle points of thermodynamics. The heat dissipated by the negative enthalpy change in the reaction to make water results in a large positive entropy change in the surroundings. In fact, the reaction to make water proceeds with explosive force. The heat dissipated in the surroundings $\Delta_r H^\ominus$ is also an entropy term. The entropy change in the surroundings is:

$$\Delta_r S_{surr}^\ominus = \frac{\Delta_r H^\ominus}{T}$$

The entropy change of the surroundings is:

$$\Delta_r S = -(-572 \text{ kJ/mol})/298 \text{ K} = + 1.92 \times 10^3 \text{ J/mol-K}$$

which is much larger than the negative entropy change of the system (-327 J/mol-K).

Question

An endothermic reaction can be spontaneous if:

- A. $\Delta S > 0$
- B. $\Delta S < 0$
- C. $\Delta S = 0$
- D. none of the above

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