

**Temperature Dependence of Reaction Enthalpy, $\Delta_r S$**

For reaction $T_1: R \rightarrow P$:

\[ \Delta_r S_{T_1} = C_p^r \ln \frac{T_1}{T_2} + \Delta_r S_{T_1} + C_p^r \ln \frac{T_2}{T_1} \]

For reaction $T_2: R \rightarrow P$:

\[ \Delta_r S_{T_2} = \Delta_r S_{T_1} + (C_p^{pr} - C_p^{r}) \ln \frac{T_2}{T_1} \]

\[ \Delta_r S_{T_2} = \Delta_r S_{T_1} + \Delta_r C_p \ln \frac{T_2}{T_1} \]

\[ \Delta_r C_p = C_p^{pr} - C_p^{r} \]

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**The Third Law and Chemistry**

Is $S_0$ really equal to zero for all perfect crystalline compounds?

Simple example: What about different crystalline forms?

Let us assume $S_0 = 0$ for perfect rhombic sulfur ($S_8$) and determine experimentally $S_0$ for monoclinic sulfur, to see how the third law is followed.

$S($rhombic$) \rightarrow S($monoclinic$) \quad \Delta_{tr}H = 401.7 \text{ J mol}^{-1} \text{ at } 368.5 \text{ K} \quad \Delta_r S = ? \text{ at } 0 \text{ K.}$

\[ \Delta_{tr}S = \frac{401.7 \text{ J mol}^{-1}}{368.5 \text{ K}} = 1.09 \pm 0.01 \text{ J K}^{-1} \text{mol}^{-1} \text{ at } 368.5 \text{ K} \]

<table>
<thead>
<tr>
<th>rhombic</th>
<th>monoclinic</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_r S_{T_1}$</td>
<td>$\Delta_{tr}S_0$ = $36.86 \pm 0.2$ J K$^{-1}$mol$^{-1}$</td>
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is this result zero?