Entropy Change Due to Mixing of Ideal Gases

To calculate entropy of mixing, ΔS, treat the process as two separate, isothermal gas expansions.

$$\Delta S_A = n_A R \ln \left(\frac{V_A + V_B}{V_A} \right) \qquad \Delta S_B = n_B R \ln \left(\frac{V_A + V_B}{V_B} \right)$$

Then

$$\Delta S_{mix} = \Delta S_A + \Delta S_B = n_A R \ln \left(\frac{V_A + V_B}{V_A} \right) + n_B R \ln \left(\frac{V_A + V_B}{V_B} \right)$$

Then by Avogadro's law, $V \propto n$ at constant T and P.

$$\Delta S_{mix} = -R(n_A \ln(\chi_A) + n_B \ln(\chi_B))$$

Since χ_A and χ_B are mole fractions of A and B respectively and their values are less than 1, it follows that $\Delta S_{mix} > 0$.

For isothermal expansion of an ideal gas:

$$\Delta S = n R \ln \left(\frac{V_2}{V_1} \right)$$

The heat absorbed by an ideal gas in an isothermal expansion is

$$q_{rev} = n R T \ln \left(\frac{V_2}{V_1} \right)$$

Therefore,

$$\frac{q_{rev}}{T} = n R \ln \left(\frac{V_2}{V_1} \right) \Rightarrow \Delta S = \frac{q_{rev}}{T}$$

This equation is true for any *reversible process* occurring at *constant temperature*.

Recall that

$$dq_{rev} = dU - dW_{rev} = C_V dT + P dV = C_V dT + \frac{nRT}{V} dV$$

Note that

$$\frac{\partial C_V}{\partial V} \neq \frac{\partial}{\partial T} \frac{nRT}{V}$$

q is not a state function, and so the mixed second partial derivatives are not equal. Dividing both sides by T

$$\frac{\partial}{\partial V} \left(\frac{C_V}{T} \right) = \frac{\partial}{\partial T} \left(\frac{nR}{V} \right)$$

Then

$$\Delta S(V, T) = \int dS = \int \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{C_V}{T} dT + \int_{V_1}^{V_2} \frac{nR}{V} dV$$

Therefore,

$$\Delta S(V, T) = C_V \ln \left(\frac{T_2}{T_1} \right) + n R \ln \left(\frac{V_2}{V_1} \right)$$

Example 1. One mole of N_2 at 20.5°C and 6.00 bar undergoes a transformation to the state described by 145°C and 2.75 bar. Calculate ΔS if

$$C_{P,m} = 30.81 - (11.87 \times 10^{-3})T + (2.3968 \times 10^{-5})T^2 - (1.0176 \times 10^{-8})T^3$$

Solution:

$$\Delta S = -\ln\left(\frac{2.75}{6.00}\right) + \int_{293}^{418} \frac{30.81 - (11.87 \times 10^{-3})T + (2.3968 \times 10^{-5})T^2 - (1.0176 \times 10^{-8})T^3}{T}dT$$

$$= 6.48 + \left[30.81\ln T - 11.87 \times 10^{-3}T + \frac{2.3969 \times 10^{-5}}{2}T^2 - \frac{1.0176 \times 10^{-8}}{3}T^3\right]_{293}^{418}$$

$$=$$

Consider entropy change for the following processes:

- Increase volume of a gas: $nR\ln\left(\frac{V_2}{V_1}\right)$, $\Delta S > 0$.

- Compression of a gas: $nR\ln\left(\frac{V_2}{V_1}\right)$, $\Delta S < 0$.

- T increased at constant P: $nC_P\ln\left(\frac{T_2}{T_1}\right)$, $\Delta S > 0$

- T decreases at constant P: $nC_P\ln\left(\frac{T_2}{T_1}\right)$, $\Delta S < 0$.
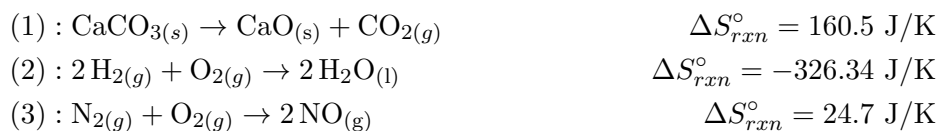
In isolated systems:

1. $\Delta S > 0$ for the spontaneous process direction.

2. $\Delta S < 0$ for the nonspontaneous process direction.

3. $\Delta S = 0$ for a reversible process.

Condition: System does not exchange energy with surroundings in the form of heat or work. This is due to the changes in the surroundings produce entropy changes in the surroundings.

$$\Delta S_{sys} + \Delta S_{sur} > 0$$

For example, consider the three reactions given below:

$$(1): CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \qquad\qquad \Delta S^{\circ}_{rxn} = 160.5 \text{ J/K}$$
$$(2): 2\,H_{2(g)} + O_{2(g)} \rightarrow 2\,H_2O_{(l)} \qquad\qquad \Delta S^{\circ}_{rxn} = -326.34 \text{ J/K}$$
$$(3): N_{2(g)} + O_{2(g)} \rightarrow 2\,NO_{(g)} \qquad\qquad \Delta S^{\circ}_{rxn} = 24.7 \text{ J/K}$$

Consider the reaction to produce water. The entropy is very negative because the net number of gas molecules decrease and we are producing a liquid from gases. One would except that this reaction would not occur. But don't forget we have only considered the entropy of the system. But what about the entropy of the surroundings?

Besides the system, we also have to consider the surroundings.

- The system is much smaller compared to the surroundings.

- Surroundings is an infinitely large reservoir.

- Any heat or work exchanged between system and surroundings can only alter the properties of the surrounds by an infinitesimal amount.

Remember that infinitesimal changes are characteristic of reversible processes. We can forget the path, and so
$$\Delta S_{sur} = \frac{q_{sur}}{T_{sur}}$$
Consider again the isothermal expansion of an ideal gas, where we said that the heat absorbed by the system is
$$q_{sys} = nRT \ln\left(\frac{V_2}{V_1}\right)$$
so heat lost by the surroundings is
$$q_{sur} = -nRT \ln\left(\frac{V_2}{V_1}\right)$$
Therefore,
$$\Delta S = \Delta S_{sys} + \Delta S_{sur} = 0$$
for a reversible process.

Yet since no work is done in the process there is no heat exchange between system and surroundings.
$$q_{sur} = 0 \qquad \Delta S_{sur} = 0$$
Therefore,
$$\Delta S_{uni} = nRT \ln\left(\frac{V_2}{V_1}\right) + 0 > 0$$

1. For a *reversible* process: $\Delta S_{uni} = 0$

2. For an *irreversible* process: $\Delta S_{uni} > 0$.

3. Overall, $\Delta S_{uni} \geq 0$.

Example 2. One mole of an ideal gas at 25°C is allowed to expand adiabatically and irreversibly from 1 L to 10 L with no work done. What is the final temperature of the gas? Calculate the values of ΔS_{sys}, ΔS_{sur}, ΔS_{uni}.

Solution: $\Delta U = 0$ as temperature does not change for a free expansion. ΔS must be calculated from a reversible process:
$$\Delta S_{sys} = nR \ln\left(\frac{V_2}{V_1}\right) = (8.314) \ln\left(\frac{10.0}{1.0}\right) = 19.1 \text{ J/mol K}$$
$$\Delta S_{sur} = 0$$
$$\Delta S_{uni} = 19.1 \text{ J/mol K}$$

Entropy Change Due to Phase Transitions

Entropy increases when going from a solid to a liquid since the number of possible states for molecules increases.

1. The heat of fusion $\Delta_{fus}\Delta H$. For example,

$$\Delta_{fus}S^\circ(\text{H}_2\text{O}) = 22 \text{ J/mol K}$$

2. Heat of Vaporization $\Delta_{vap}\Delta H$. For example,

$$\Delta_{vap}S^\circ(\text{H}_2\text{O}) = 109.0 \text{ J/mol K}$$

In genera, $\Delta_{vap}S^\circ > \Delta_{fus}S^\circ$ for the same substance. Solid to liquid transitions result in a relatively small increase in molecular disorder. Arrangement of molecules in gaseous state is completely random. Liquid to vapor transition, large increase in disorder.
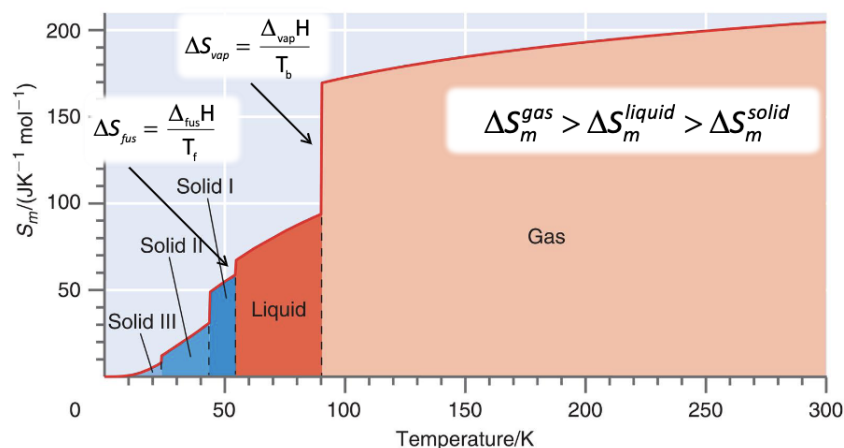
The molar entropy of O_2 is shown as a function of temperature. The vertical dashed lines indicate constant temperature-phase transitions.

Recall that S for phase transitions:

$$\Delta S_{sys} = \frac{\Delta H_{trans}}{T_{trans}}$$

Here, we are calculating the entropy change for the system. Heat is absorbed reversibly in an equilibrium process so the changes in entropy for the surroundings at a phase transition will be given by

$$\Delta S_{sur} = -\frac{\Delta H_{trans}}{T_{trans}}$$

Therefore, the total change in entropy for the universe will be zero.

Example 3. Calculate ΔS when a sample of one mole of $\text{H}_2\text{O}_{(l)}$ is heated from 25°C to 100°C, and then following vaporization, the $\text{H}_2\text{O}_{(g)}$ is further heated to 160°C.

Solution:

$$\Delta S = C_P(\text{H}_2\text{O}) \ln\left(\frac{373}{298}\right) + \frac{\Delta H_{vap}}{373} + C_P(\text{H}_2\text{O}_{(g)}) \ln\left(\frac{433}{373}\right)$$

Third Law of Thermodynamics

The third law of thermodynamics states that the entropy of a perfect crystal at 0 K is zero. The third law provides the reference state for use in calculating absolute entropies.

For a crystal at $T = 0$ k, perfectly oriented, and for one mole of molecules, there is only one microstate at $T = 0$ and so

$$\mathcal{W} = 1^{6.02 \times 10^{23}} = 1$$

and

$$S = k \ln 1 = 0 \Rightarrow \lim_{T \to 0} S = 0$$

For a crystal at $T > 0$ K, randomly oriented, thermal motion contributes to the entropy of the substance so that it is no longer zero.

$$\mathcal{W} > 1 \qquad S > 0$$

and

$$\lim_{T \to 0} C_P = \lim_{T \to 0} C_V = 0$$

Absolute Entropy

Entropy defined experimentally using

$$q_{rev,P} = C_P dT$$

plus the contribution from fusion or vaporization.

$$S(T)_{(g)} = S(0) = \int_0^{T_{fus}} \frac{C_{P,(s)}}{T} dT + \frac{\Delta H_{fus}}{T_{fus}} + \int_{T_{fus}}^{T_{boil}} \frac{C_{P,(l)}}{T} dT + \frac{\Delta H_{vap}}{T_{boil}} + \int_{T_{boil}}^{T_{final}} \frac{C_{P,(g)}}{T} dT$$

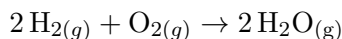Entropy values tabulated at 298.15 K and 1 bar. What if not at 298 K?

$$\Delta S^T = \Delta S_{298.15}^\circ + \int_{298}^T \frac{n \Delta C_P}{T} dT = \Delta S_{298.15}^\circ + n C_P \ln \left(\frac{T}{298.15} \right)$$

We can also keep track of entropy changes in a reaction by subtracting S_p° from S_r°.

$$\Delta_r S^\circ = \sum_{p \in \mathcal{P}} \nu_p S_p^\circ - \sum_{r \in \mathcal{R}} \nu_r S_r^\circ$$

where ν are coefficients from balanced chemical equation.

Example 4. Calculate the entropy change for the formation of water vapor at 298 K.

$$2\,H_{2(g)} + O_{2(g)} \to 2\,H_2O_{(g)}$$

where $S_{H_2}^\circ = 130.57$ J/mol K, $S_{O_2}^\circ = 205.04$ J/mol K, and $S_{H_2O}^\circ = 188.72$ J/mol K.

Solution:

$$\Delta S^\circ(25°C) = 2S_{H_2O}^\circ - S_{H_2}^\circ - S_{O_2}^\circ = 2(188.72) - 130.57 - 205.04 = -88.74 \text{ J/K}$$

Example 5. If a spark is applied to a mixture of $H_{2(g)}$ and $O_{2(g)}$ an explosion occurs and water is formed. The gaseous water is cooled to 100°C. Calculate the entropy change when 2 mol of gaseous H_2O is formed at 100°C and 1 atom from $H_{2(g)}$ and $O_{2(g)}$ at the same temperature and each at a particular pressure of 1 atm.

$$2\,H_{2(g)} + O_{2(g)} \rightarrow 2\,H_2O_{(g)}$$
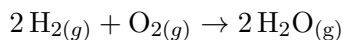
Solution: From Example 4, we found that $\Delta S°(25°C) = -88.74$ J/K. To find ΔS at 100°C and 1 atm, we need to know the heat capacities of the reactants and products.

$$\Delta C_P°(25) = 2C_{P,H_2O} - C_{P,O_2} - 2C_{P,H_2} = 2(33.6) - 39.4 - 2(28.8) = -19.8 \text{ J/K}$$

Then

$$\Delta S°(100) = \Delta S°(25) + \int_{298}^{373} \frac{C_P(25)}{T} dT = -88.74 - 19.8 \ln\left(\frac{373}{298}\right) = -93.18 \text{ J/K}$$

Example 6. Consider the reaction and calculate the entropy of the reaction mixture, surroundings, and the universe at 298 K. Why is the result reassuring to Earth's inhabitants?

$$N_{2(g)} + O_{2(g)} \rightarrow 2\,NO_{(g)}$$
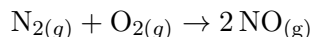
Use the values $\Delta H_f°(NO_{(g)}) = 90.4$ kJ/mol, $S°(N_{2(g)}) = 191.6$ J/mol K, $S°(O_{2(g)}) = 205.0$ J/mol K, and $S°(NO_{(g)}) = 210.6$ J/mol K.

Solution: Exercise. (Answer: $\Delta S_{sur} = -607$ J/mol K, $\Delta S_{uni} = -582$ J/mol K)