# Lecture-3

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## 5. Constant-pressure heating with no phase change

First, suppose the heating is done *reversibly*. At constant pressure (provided no phase change occurs),

$$dq_{\text{rev}} = dq_P = C_P\, dT$$

$$\Delta S = \int_1^2 dq_{\text{rev}}/T = \int_{T_1}^{T_2} \frac{C_P}{T}\, dT \qquad \text{const. } P\text{, no phase change}$$

$$= C_P \ln (T_2/T_1)$$

# Example: $\Delta S$ for heating at constant $P$

The specific heat capacity $c_P$ of water is nearly constant at 1.00 cal/(g °C) in the temperature range 25°C to 75°C at 1 atm. Find $\Delta S$ when 100 g of water is reversibly heated from 25°C to 50°C at 1 atm.

The system's heat capacity is $C_P = mc_P = (100\ \text{g})[1.00\ \text{cal/(g °C)}] = 100\ \text{cal/K}$. (A temperature change of one degree Celsius equals a change of one kelvin.) For the heating process, with $C_P$ constant gives

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{C_P}{T}\, dT = C_P \ln \frac{T_2}{T_1}$$

$$= (100\ \text{cal/K}) \ln \frac{323\ \text{K}}{298\ \text{K}} = 8.06\ \text{cal/K} = 33.7\ \text{J/K}$$

**Exercise**

Find $\Delta S$ when 100 g of water is reversibly heated from 50°C to 75°C at 1 atm. (*Answer:* 31.2 J/K.)

## 6. **Reversible change of state of a perfect gas**

From the first law, we have for a reversible process in a perfect gas

$$dq_{\text{rev}} = dU - dw_{\text{rev}} = C_V\,dT + P\,dV = C_V\,dT + nRT\,dV/V$$

$$dS = dq_{\text{rev}}/T = C_V\,dT/T + nR\,dV/V$$

$$\Delta S = \int_1^2 C_V(T)\,\frac{dT}{T} + nR\int_1^2 \frac{dV}{V}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V(T)}{T}\,dT + nR\ln\frac{V_2}{V_1} \qquad \text{perf. gas}$$

# Reversible change of state of a perfect gas

- If $T_2 > T_1$, the first integral is positive, so increasing the temperature of a perfect gas increases its entropy.
- If $V_2 > V_1$, the second term is positive, so increasing the volume of a perfect gas increases its entropy.
- If the temperature change is not large, it may be a good approximation to take $C_V$ constant, in which case
- $\Delta S \approx C_V \ln (T_2/T_1) + nR \ln (V_2/V_1)$.
- A mistake students sometimes make in using the is to write $\ln (V_2/V_1) = \ln (P_1/P_2)$, forgetting that $T$ is changing. The correct expression is $\ln (V_2/V_1) = \ln (P_1T_2/P_2T_1)$.

## 7. Irreversible change of state of a perfect gas

Let $n$ moles of a perfect gas at $P_1$, $V_1$, $T_1$ irreversibly change its state to $P_2$, $V_2$, $T_2$. We can readily conceive of a reversible process to carry out this same change in state.

Since $S$ is a state function, $\Delta S$ for this reversible change from state 1 to state 2 is the same as $\Delta S$ for the irreversible change from state 1 to state 2, even though $q$ is not necessarily the same for the two processes.

Therefore $\Delta S$ for the irreversible change is-

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V(T)}{T}\, dT + nR \ln \frac{V_2}{V_1}$$

# Example: **$\Delta S$ for expansion into a vacuum**

Let $n$ moles of a perfect gas undergo an adiabatic free expansion into a vacuum (the Joule experiment). (*a*) Express $\Delta S$ in terms of the initial and final temperatures and volumes. (*b*) Calculate $\Delta S_m$ if $V_2 = 2V_1$.

(*a*) The initial state is $T_1$, $V_1$, and the final state is $T_1$, $V_2$, where $V_2 > V_1$. $T$ is constant because $\mu_J = (\partial T/\partial V)_U$ is zero for a perfect gas. Although the process is adiabatic ($q = 0$), $\Delta S$ is not zero because the process is irreversible.

In this case, $\Delta S = nR \ln(V_2/V_1)$, since the temperature integral is zero when $T_2 = T_1$.

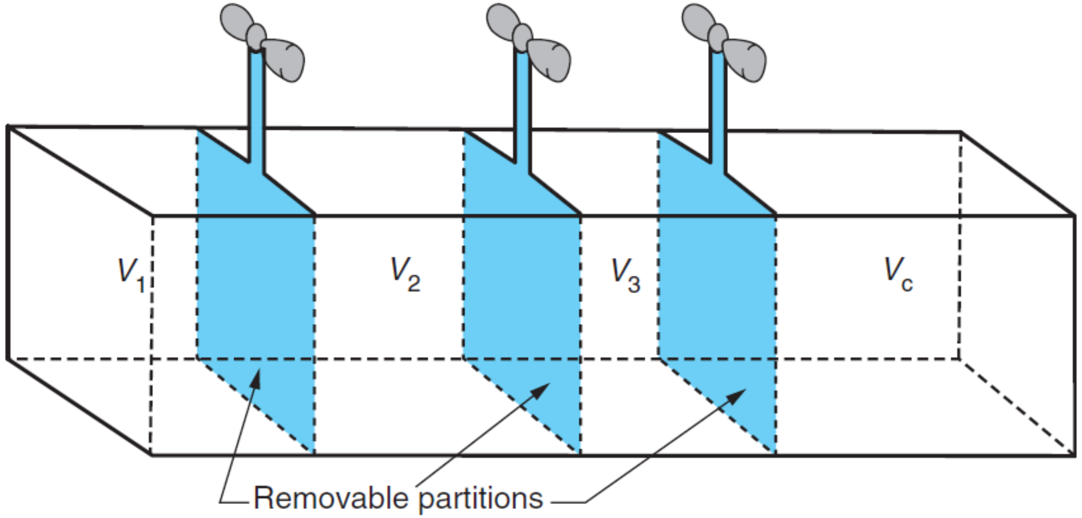
(*b*) If the original container and the evacuated container are of equal volume, then $V_2 = 2V_1$ and $\Delta S = nR \ln 2$. We have

$$\begin{aligned}\Delta S/n = \Delta S_m &= R \ln 2 \\ &= [8.314 \text{ J/(mol K)}](0.693) = 5.76 \text{ J/(mol K)}\end{aligned}$$

# 8. Entropy of Mixing of Ideal Gases

Consider a mixture of several ideal gases in which $n_1$ is the amount of substance *1*, $n_2$ is the amount of substance *2*, and so on. The number of substances is denoted by *s*.

In an initial state each substance confined in a separate compartment of a container, as shown in the figure.



***Reference:** Physical Chemistry- R.G. Mortimer*

The system is so arranged that each gas is at the temperature and the pressure of the final mixture.

The volume of each component is denoted by $V_i$:

$$V_i = \frac{n_i RT}{P} \quad (i = 1, 2, 3, \ldots, s)$$

The total volume of the container is denoted by *V:*

$$V = \sum_{i=1}^{s} V_i$$

***Reference:*** *Physical Chemistry- R.G. Mortimer*

The entropy changes of the individual gases are given by

$$\Delta S_i = n_i R \ln\left(\frac{V}{V_i}\right) \quad (i = 1, 2, 3, \ldots, s)$$

The entropy change of the system is the sum of these quantities:

$$\Delta S = \sum_{i=1}^{s} n_i R \ln\left(\frac{V}{V_i}\right)$$

***Reference:*** *Physical Chemistry- R.G. Mortimer*

# Expression of $\Delta S$ in terms of mole fractions

The mole fraction substance number *i* is defined by

$$x_i = \frac{n_i}{n} = \frac{PV_i/RT}{PV/RT} = \frac{V_i}{V}$$

(where *n* is the total amount of all gases)

Therefore,

$$\Delta S_{\mathrm{mix}} = R\sum_{i=1}^{s} n_i \ln(1/x_i) = -R\sum_{i=1}^{s} n_i \ln(x_i)$$

***Reference:*** *Physical Chemistry- R.G. Mortimer*

## Example

Assume that 1.000 mol of dry air consists of 0.780 mol of nitrogen, 0.210 mol of oxygen, and 0.010 mol of argon. Find the entropy change of mixing of 1.000 mol of dry air. Disregard the fact that each substance has more than one isotope.

## Solution

$$
\begin{aligned}
\Delta S &= -(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\big[(0.780\,\mathrm{mol})\ln(0.780) \\
&\qquad + (0.21\,\mathrm{mol})\ln(0.210) + (0.01\,\mathrm{mol})\ln(0.01)\big] \\
&= 4.72\,\mathrm{J\,K^{-1}}
\end{aligned}
$$

***Reference:*** *Physical Chemistry- R.G. Mortimer*

# Calculation of Entropy Change: Summary

1. Cyclic process, $\Delta S = 0$

2. Reversible adiabatic process, $\Delta S = 0$

3. Reversible phase change at constant $T$ and $P$, $\Delta S = \dfrac{\Delta H}{T}$

4. Reversible isothermal process, $\Delta S = q_{\text{rev}}/T$

5. Constant-pressure heating with no phase change, $\Delta S = C_p \ln(T_2/T_1)$

6. Reversible/ Irreversible change of state of a perfect gas

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V(T)}{T}\, dT + nR \ln \frac{V_2}{V_1}$$

7. Entropy of Mixing of Ideal Gases

$$\Delta S_{\text{mix}} = R \sum_{i=1}^{s} n_i \ln(1/x_i) = -R \sum_{i=1}^{s} n_i \ln(x_i)$$