# Gibbs Equation

## 1 Overview

Recall the second law for CM, we can relate entropy changes to heat transfer and irreversibility:

$$dS = \frac{\delta Q}{T} + \delta P_s \tag{1}$$

But entropy is a TD property, we want to relate S changes to changes in other TD properties. Therefore, we need to find a generally applicable state equation.

## 2 Gibbs Equation

### 2.1 Derivation

Recall the first law:

$$de = \delta q + \delta w \tag{2}$$

If we only consider internal energy, and the only reversible work mode is compression/expansion:

$$du = \delta q - pdv \tag{3}$$

If we assume the process is reversible, based on second law:

$$ds = \delta q/T \tag{4}$$

Plug back in, we get:

$$du = Tds - pdv \tag{5}$$

Solve $ds$, we get the **Gibbs Equation:**

$$ds = \frac{du}{T} + \frac{p}{T}dv \tag{6}$$

Recall the definition of enthalpy:

$$dh = du + pdv + vdp \tag{7}$$

We get another version of **Gibbs Equation:**

$$ds = \frac{dh}{T} - \frac{v}{T}dp \tag{8}$$

## 2.2 State Equations

During the derivation, we assume **reversible process with only compression/expansion work.** However, these expressions **are valid not only under these conditions, but generally applicable,** since they only involve **state properties**, they are **state equations**.

## 2.3 For Ideal Gases

Start from original Gibbs Equation:

$$ds = \frac{du}{T} + \frac{p}{T}dv \tag{9}$$

Recall that:

$$du = c_v dT \tag{10}$$

$$pv = RT \tag{11}$$

So we have:

$$ds = \frac{c_v dT}{T} + \frac{R}{v}dv \tag{12}$$

If we integrate this:

$$\int_{s_1}^{s_2} ds = \int_{T_1}^{T_2} \frac{c_v dT}{T} + \int_{v_1}^{v_2} \frac{R}{v}dv \tag{13}$$

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_v dT}{T} + R\int_{v_1}^{v_2} \frac{dv}{v} \tag{14}$$

Finally we have:

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_v dT}{T} + Rln\frac{v_2}{v_1} \tag{15}$$

Or:

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_v dT}{T} - Rln\frac{\rho_2}{\rho_1} \tag{16}$$

Similarly, we can use enthalpy version:

$$ds = \frac{dh}{T} - \frac{v}{T}dp = \frac{c_p dT}{T} - \frac{R}{p}dp \tag{17}$$

Integrate:

$$\int_{s_1}^{s_2} ds = \int_{T_1}^{T_2} \frac{c_p dT}{T} - R\int_{p_1}^{p_2} \frac{dp}{p} \tag{18}$$

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_p dT}{T} - Rln\frac{p_2}{p_1} \tag{19}$$

**Notice that the dependencies of entropy respect to T, p and $\rho$ are separate.**

## 2.4 For Carlorically Perfect Gas

Under CPG assumption, specific heat is constant. Therefore, we have:

$$s_2 - s_1 = c_v ln\frac{T_2}{T_1} + Rln\frac{v_2}{v_1} \tag{20}$$

$$s_2 - s_1 = c_v ln\frac{T_2}{T_1} - Rln\frac{\rho_2}{\rho_1} \tag{21}$$

$$s_2 - s_1 = c_p ln\frac{T_2}{T_1} - Rln\frac{p_2}{p_1} \tag{22}$$

Normalization:

$$\frac{\Delta s_{12}}{R} = \frac{c_p}{R}ln\frac{T_2}{T_1} - ln\frac{p_2}{p_1} = ln(\frac{T_2}{T_1})^{c_p/R} - ln\frac{p_2}{p_1} \tag{23}$$

Recall that:

$$\frac{c_p}{R} = \frac{\gamma}{\gamma - 1} \tag{24}$$

$$\frac{c_v}{R} = \frac{1}{\gamma - 1} \tag{25}$$

Therefore:

$$\frac{\Delta s_{12}}{R} = ln(\frac{T_2}{T_1})^{\frac{\gamma}{\gamma-1}} - ln\frac{p_2}{p_1} = ln(\frac{T_2}{T_1})^{\frac{1}{\gamma-1}} - ln\frac{\rho_2}{\rho_1} \tag{26}$$

# 3 Isentropic Relations

## 3.1 TPG

At first, **we assume TPG, which means specific heat is a function of temperature.** For simplification, we define:

$$s_1^o = \int_{T_{ref}}^{T_1} \frac{c_p dT}{T} \tag{27}$$

$$s_2^o = \int_{T_{ref}}^{T_2} \frac{c_p dT}{T} \tag{28}$$

$$\Delta s_{12}^o(T) = s_2^o - s_1^o \tag{29}$$

For isentropic process, $\Delta s = 0$. Therefore:

$$0 = \int_{T_1}^{T_2} \frac{c_p dT}{T} - Rln\frac{p_2}{p_1} \tag{30}$$

$$ln\frac{p_2}{p_1} = \frac{1}{R}\int_{T_1}^{T_2} \frac{c_p dT}{T} \tag{31}$$

Finally we have:

$$\frac{p_2}{p_1} = e^{\frac{1}{R}\int_{T_1}^{T_2}\frac{c_p dT}{T}} = e^{\frac{\Delta s_{12}^o(T)}{R}} \tag{32}$$

In terms of specific volume, recall that:

$$\frac{v_1}{v_2} = \frac{T_1/p_1}{T_2/p_2} = \frac{T_1}{T_2}\frac{p_2}{p_1} \tag{33}$$

Therefore:

$$\frac{v_1}{v_2} = \frac{\rho_2}{\rho_1} = \frac{T_1}{T_2}e^{\frac{\Delta s_{12}^o(T)}{R}} \tag{34}$$

## 3.2 CPG

Now, the specific heat is a constant, then:

$$0 = c_p ln\frac{T_2}{T_1} - Rln\frac{p_2}{p_1} \tag{35}$$

$$\frac{p_2}{p_1} = (\frac{T_2}{T_1})^{\frac{c_p}{R}} = (\frac{T_2}{T_1})^{\frac{\gamma}{\gamma-1}} \tag{36}$$

$$0 = c_v ln\frac{T_2}{T_1} - Rln\frac{\rho_2}{\rho_1} \tag{37}$$

$$\frac{\rho_2}{\rho_1} = (\frac{T_2}{T_1})^{\frac{c_v}{R}} = (\frac{T_2}{T_1})^{\frac{1}{\gamma - 1}} \tag{38}$$

**Therefore we have the power law of isentropic process:**

$$\frac{\rho_2}{\rho_1} = (\frac{p_2}{p_1})^{\frac{1}{\gamma}} \tag{39}$$

$$\frac{p}{\rho^\gamma} = pv^\gamma = const \tag{40}$$

## 3.3 Polytropic Process

We define the general form as polytropic process:

$$pv^n = constant \tag{41}$$

Then we have the following conditions:

1. $n = 0$: Isobaric
2. $n = 1$: Isothermal
3. $n = \gamma$: Isentropic
4. $n = \infty$: Isochoric

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