**Lapse Rate. Prof. Ruiz (Doc), UNC-Asheville (1978-2021), DoctorPhys on YouTube.**
**Prerequisites: Chemistry, Physics I, II. Calculus I, II, III. Thermodynamics.**

**Chapter K. Gibbs Free Energy.** State variables describe equilibrium states of thermodynamic systems. An equilibrium state is one where a unique pressure applies to all regions of the gas. The same goes for the temperature. State variables are also state functions. But historically, the description state function has been used for state variables such as energy and entropy. In this section we introduce two more state functions, the Gibbs free energy and the Helmholtz free energy. We will work with specific values.

## 1. Review of Energy and Enthalpy.

The first law of thermodynamics can be written as

$$du = \delta q - pd\alpha \, .$$

But we also have the entropy equation $ds = \frac{\delta q}{T}$, our Equation (17).

We then can write $\delta q = Tds$, which is analogous to $\delta q = pd\alpha$.

In a sense, we now have a combined 1st and 2nd law.

$$du = Tds - pd\alpha$$

Our Equation (14) is $\delta q = dh - \alpha dp$, which we can write as

$Tds = dh - \alpha dp$, which leads to $dh = Tds + \alpha dp$.

In the table below we list the state functions energy and entropy and give their differential forms. But remember that all the state functions are variables and the variables are state functions. The distinction below is historical.

| State Function Name | Function Symbol | Differential | Variables |
|---|---|---|---|
| energy | $u$ | $du = Tds - pd\alpha$ | $s, \alpha$ |
| enthalpy | $h = u + p\alpha$ | $dh = Tds + \alpha dp$ | $s, p$ |

Notice how we have $pd\alpha$ in $du$ and $\alpha dp$ in $dh$. The variables $p$ and $\alpha$ are switched. The table suggests the construction of state functions where $T$ and $s$ are switched: $Tds \rightarrow sdT$. We can easily accomplish this switch using $Tds = d(Ts) - sdT$. We will be rewarded big time!

Let's first try this switch starting in $du = Tds - pd\alpha$. Then, we will consider $dh = Tds + \alpha dp$.

We begin with $du = Tds - pd\alpha$ and substitute $Tds = d(Ts) - sdT$ .

$$du = d(Ts) - sdT - pd\alpha \quad \Rightarrow \quad du - d(Ts) = -sdT - pd\alpha \quad \Rightarrow \quad d(u - Ts) = -sdT - pd\alpha$$

We define a new function $\boxed{f \equiv u - Ts}$, called the Helmholtz free energy.

Next, we work with $dh = Tds + \alpha dp$, again using $Tds = d(Ts) - sdT$.

$$dh = d(Ts) - sdT + \alpha dp \quad \Rightarrow \quad dh - d(Ts) = -sdT + \alpha dp \quad \Rightarrow \quad d(h - Ts) = -sdT + \alpha dp$$

We define another new function $\boxed{g \equiv h - Ts}$, which is called the Gibbs free energy.

Since $h = u + p\alpha$, we can also write $g = u + p\alpha - Ts$ or $g = u - Ts + p\alpha$.

Our results are summarized in the table below.

| State Function Name | Function Symbol | Differential | Variables |
|---|---|---|---|
| specific energy | $u$ | $du = Tds - pd\alpha$ | $s, \alpha$ |
| specific enthalpy | $h = u + p\alpha$ | $dh = Tds + \alpha dp$ | $s, p$ |
| specific Helmholtz free energy | $f = u - Ts$ | $df = -sdT - pd\alpha$ | $T, \alpha$ |
| specific Gibbs free energy | $g = u - Ts + p\alpha$ | $dg = -sdT + \alpha dp$ | $T, p$ |

The Gibbs free energy is very convenient for us since during a phase transition, the temperature and pressure are constant. Therefore, for liquid water evaporating or water vapor condensing into liquid we have $dg = -sdT + \alpha dp = 0$ since $dT = 0$ and $dp = 0$.

Historically, the term "free energy" emerged to mean the available energy for useful work at constant temperature. Refer to the Helmholtz free energy where we find $df = (-sdT - pd\alpha) = -pd\alpha$ for $dT = 0$. The Helmholtz free energy decreases by an equal amount $pd\alpha$ as the gas does work $pd\alpha$ on its environment by expanding. Since the Gibbs function $g = u - Ts + p\alpha$ can also be written as $g = f + p\alpha$, where $f$ is the Helmholtz free energy, the free-energy name is also attached to the Gibbs function. This particular nomenclature is not very useful for us. The important observation is that the change in the Gibbs function is zero for a phase transition, which takes place at constant temperature and pressure. From the above table we can now add two more formulas to our growing list.

(20) $\boxed{g = u - sT + p\alpha}$ (21) $\boxed{dg = -sdT + \alpha dp}$