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Is Gibbs Energy Truly a Form of Energy?

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Abstract

The article shows that the Gibbs energy (free energy) is not energy and that work is done due to the heat of the environment, not the Gibbs energy. The change in Gibbs energy at constant values of temperature and pressure in most cases was explained by the performance of work due to Gibbs energy. Gibbs energy has the dimension of energy and this forces many to believe that Gibbs energy is energy. However, work is actually performed due to the heat of the environment in an amount equal to the change in Gibbs energy. If $\Delta G < 0$, then the process can be used for another process. A decrease in G at constant values of T and p leads the system to equilibrium when $\Delta G = 0$.

Keywords: Gibbs energy; enthalpy; irreversible process; reversible process; useful work

Introduction

According to the IUPAC definition Gibbs energy (function), G: Enthalpy minus the product thermodynamic temperature and entropy [1]

$$G = H - TS \quad (1)$$

It was formerly called free energy or free enthalpy [1]. Let us consider in more detail the origin of the Gibbs function.

The sum of the kinetic energy of all molecules in a system can be considered the internal energy (U). The change in internal energy occurs due to interaction with the external environment and this change can be represented as follows

$$\Delta U = q + w \quad (2)$$

where ΔU is the change in internal energy, q is the heat entering the system, w is the work of the external environment on the system. Work is usually represented as the sum of two components: the work of expanding the entire system

$$w_{\text{exp}} = -pdV \quad (3)$$

and the rest of the work, which is called useful W_{useful}. Now equation (2) can be written as follows

$$\Delta U = \Delta q - pdV + \delta w_{\text{useful}} \quad (4)$$

If there is no useful work, then in the case of an isobaric process (p=Const) from (4) we obtain

$$\delta q = d(U + pV) = dH \quad (5)$$

where the quantity H is called enthalpy. The change in enthalpy at constant pressure is equal to the heat supplied to the system. In a reversible process the change in entropy of the system is equal

$$dS = \frac{\delta q}{T} \quad (6)$$

The equation (4) in the absence of useful work can be written as

$$dU = TdS - pdV \quad (7)$$

For dH from (5) we obtain

$$dH = TdS + Vdp \quad (8)$$

Using (7) and (8), we find

$$d(H - TS) = -SdT + Vdp = dG \quad (9)$$

where

$$G = H - TS \quad (10)$$

Gibbs energy (function). The change in the Gibbs function with pressure for an ideal gas at a constant temperature is found from (9)

$$dG_T = Vdp = \frac{RT}{p}dp \quad \text{and} \quad G_T \approx RT \ln p \quad (11)$$

Gibbs energy has the dimension of energy, but is this enough to consider it as real energy?. The posing of this question at first glance seems completely meaningless, since the question was settled more than a hundred years ago. The vast majority of scientists believe that the Gibbs energy is energy [2, 3] and that useful isothermal reversible work at constant pressure and temperature is performed at its expense. Nevertheless, a number of publications express the opposite point of view [4 - 7]. Why are there different points of view? The fact is that the Gibbs energy correctly allows to calculate the amount of useful work, but this does not mean that the useful work is performed directly at its expense. The notion that isothermal reversible work is performed at expense of Gibbs energy hinders the development of understanding of chemical and, especially, biological processes. Why did opposite points of view not develop? The fact is that the most authors [4, 5] did not demonstrate, what is the real source of energy for doing the work.

Consider the change in the Gibbs energy at constant values of temperature and pressure

$$\Delta G_{T,p} = \Delta H_{T,p} - T\Delta S_{T,p} \quad (12)$$

Useful work is performed due to the heat of the system, compensated by the heat of the environment. In the case of a reversible process, heat is associated with a change in the entropy of the system [2]

$$q = T\Delta S \quad (13)$$

In the case of an isothermal reversible process at constant pressure, the change in G has the form

$$\Delta G_{T,p} = \Delta H - T\Delta S = \Delta U + \Delta(pV) - T\Delta S = q + w + \Delta(pV) - T\Delta S = \\ T\Delta S - p\Delta V - V\Delta p + w_{\text{useful}} + p\Delta V + V\Delta p - T\Delta S = w_{\text{useful}} \quad (14)$$

Thus, changing the Gibbs function at constant values of T and p represents useful work, but useful work is not done at the expense of Gibbs energy.

Our work aims to show:

1. Gibbs energy is not energy.

2. Isothermal useful work is done due to the energy of the surroundings, rather than the Gibbs energy.

Gibbs energy change in irreversible process.

Let us first consider a simple case of an irreversible process with an ideal gas.

In the case of free irreversible expansion of the ideal gas into vacuum from pressure p_{in} to pressure p_{fin}, the change in Gibbs energy is equal (11) to $\Delta G(\text{ideal gas}) = RT\ln(p_{\text{fin}}/p_{\text{in}})$. During this expansion, the temperature of the gas does not change since no work is performed in this process, $w(\text{on ideal gas}) = 0$. Therefore, the internal energy of an ideal gas also does not change, because it depends only on the temperature, $\Delta U(\text{ideal gas}) = 0$.

The internal energy of the external environment also does not change, $\Delta U(\text{environment}) = 0$, since no work has been done and $w(\text{on environment}) = 0$.

Thus, the Gibbs energy does not produce work either on the ideal gas or on the environment, and the Gibbs energy does not transform into any other type of energy. The change in Gibbs energy simply disappeared and was not preserved. Therefore, the Gibbs energy is a function, and not real energy.

Gibbs energy change in reversible process.

Now let us consider the change in the Gibbs function in a reversible process also using the example of an ideal gas. In the case of reversible expansion of the ideal gas from pressure p_{in} to pressure p_{fin}, the change in gas Gibbs energy is equal to (11) $\Delta G(\text{ideal gas}) = RT\ln(p_{\text{fin}}/p_{\text{in}}) < 0$. During this expansion the work on the gas is equal $w(\text{on ideal gas}) = RT\ln(p_{\text{fin}}/p_{\text{in}})$.

The work is equal to the change in Gibbs energy, but it is not done at the expense of Gibbs energy. In fact, the infinitesimal work δw at pressure p in this process is equal to $\delta w = -pdV$.

This infinitesimal work is performed due to the internal energy of the gas and the temperature of the gas decreases. But since the process of reversible expansion occurs at a constant temperature, the temperature of the gas is restored due to the transfer of heat from the environment. In this case, the internal energy of the environment decreases and $\Delta U(\text{environment}) = \delta w$.

As a result of the entire expansion process, the internal energy of the gas is gradually transferred to the environment, but at the same time, the internal energy of the environment is transferred to the gas. As a result, the internal energy of the gas does not change, and the internal energy of the environment decreases by the amount of work performed.

Consequently, reversible work in the external environment is carried out due to the internal energy of the external environment, but at the same time it is equal to the change in the Gibbs energy of the system. The Gibbs energy changed not as a result of useful work being performed, but as a result of a change in the state of the system. The Gibbs energy serves only to describe the state of the system. So, Gibbs energy does not do work and therefore it cannot be called energy.

Conclusion

1. Gibbs energy is not energy, which was shown using the example of an ideal gas. An ideal gas is a classical object of thermodynamics and everything that can be demonstrated on an ideal gas, similar phenomena can be observed on other objects.

2. Isothermal useful work is done due to the energy of the surroundings, rather than the Gibbs energy of the system.

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