

Gibbs–Helmholtz equation and entropy

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Abstract This short paper deals with the close relation of the Gibbs–Helmholtz (G–H) equation to entropy. It is shown that the G–H equation is readily derived from the entropy equivalent of the Gibbs function, the Massieu function. This derivation is also compared to another simple and straightforward derivation which uses mostly pure mathematical operations for multivariate functions, without revoking the Massieu function. Finally, the so-called “compensation effect” is also treated in some detail, citing a critical paper which testifies that this effect is an artefact; it simply reflects the relation between the Gibbs function, the enthalpy, and the entropy.

Keywords Physical chemistry · Thermodynamics · Gibbs–Helmholtz equation · Massieu function

ChemTexts has published a couple of papers [1, 2] concerning the Gibbs–Helmholtz (G–H) equation. Though the obvious meaning of the equation suggests a relation between the Gibbs function and the enthalpy (or Helmholtz function), these papers also suggest that the equation expresses interrelations of entropy and enthalpy.

Here, we would like to show the close connection of the G–H equation to entropy, which readily provides an alternative way for the derivation of the equation as well. In addition, we also compare this derivation to a more conventional formal mathematical one that also reveals the relationship. Finally, we also discuss in some detail the so-called “compensation effect” which relates entropy and enthalpy.

The G–H equation in one of its most substantial forms [2]

$$\left(\frac{\partial(G/T)}{\partial T}\right)_{P,\mathbf{n}} = -\frac{H}{T^2} \quad (1)$$

is an expression of the derivative of the function G/T , whose variables are the temperature T , the pressure P , and the composition vector \mathbf{n} that contain the amount of all the components constituting the thermodynamic system (G is for the Gibbs function and H for the enthalpy). For the sake of simplicity, let us drop the composition vector as a variable in further considerations, thus restraining the validity to constant composition.

The $G/T(T, P)$ function is closely related to the entropy. Let us consider the entropy function $S(U, V)$ which is the characteristic function to use in calculations of equilibria in isolated systems. The total differential of this function can be given as

$$dS = \frac{1}{T}dU + \frac{P}{T}dV. \quad (2)$$

Let us perform Legendre transformations on this function by changing the variable U to the derivative of S with respect to U (i.e., $1/T$), and similarly V to P/T (this is the analogue of transforming the function $U(S, V)$ into $G(T, P)$ using the same kind of Legendre transformations). The resulting function $Y(1/T, P/T)$ is called the *Massieu function*, and it is the entropy-based equivalent of the energy-based Gibbs function:

$$Y = S - \frac{1}{T}U - \frac{P}{T}V, \quad (3)$$

with its total differential

$$dY = -Ud\left(\frac{1}{T}\right) - Vd\left(\frac{P}{T}\right). \quad (4)$$

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It is easy to see that the Massieu function relates to the Gibbs function $G = U - TS + PV$ as $Y = -G/T$. Thus, finding the derivative of Y with respect to T would lead to the G–H equation. As a first step, let us formally write the differential form of Eq. (3):

$$dY = dS - \frac{T dU - U dT}{T^2} - \frac{T(P dV + V dP) - PV dT}{T^2}. \quad (5)$$

Let us then substitute the right side of Eq. (2) into the above expression:

$$dY = \frac{1}{T} dU + \frac{P}{T} dV - \frac{T dU - U dT}{T^2} - \frac{T(P dV + V dP) - PV dT}{T^2}. \quad (6)$$

Upon elimination of terms that sum to zero, after rearrangement, we obtain

$$dY = \frac{U + PV}{T^2} dT - \frac{V}{T} dP. \quad (7)$$

We can recognise that the first term contains the derivative of Y (i.e., of $-G/T$) with respect to T multiplied by the increment dT , and that $U + PV$ is identical with the enthalpy H , thus we can readily write

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = -\frac{H}{T^2}, \quad (8)$$

which is the G–H equation.

The above derivation of the G–H equation clearly shows the close relation of this equation to the entropy equivalent of the Gibbs function. Thus, we can recognise that it is also closely related to the temperature derivative of the energy-based Gibbs function which is $-S$. This relation is also reflected in the identity:

$$\left(\frac{\partial H}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P = C_P. \quad (9)$$

We can see that once identifying the Massieu function (which is often used in statistical thermodynamics), an easy three-step derivation leads to the G–H equation.

However, a more formal and only slightly more complicated way of the derivation of the G–H equation also shows the relation of this equation to entropy. Let us start with a formal derivation of the function G/T considering it as a ratio of the functions G and T :

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = \frac{T \left(\frac{\partial G}{\partial T}\right)_P - G \left(\frac{\partial T}{\partial T}\right)_P}{T^2}. \quad (10)$$

Let us substitute unit for the derivative in the second term and factor out $1/T$:

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = \frac{1}{T} \left(\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T} \right). \quad (11)$$

Recalling that the partial derivative of the $G(T, P)$ function with respect to T is $-S$, we can substitute it in the form derived from the definition $G = U - TS + PV = H - TS$ as

$$-S = \frac{G - H}{T}, \quad (12)$$

thus obtaining the equation

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = \frac{1}{T} \left(\frac{G - H}{T} - \frac{G}{T} \right), \quad (13)$$

which readily leads to the G–H equation in the usual form:

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = -\frac{H}{T^2}. \quad (14)$$

Finally, let us write a few words also about the entropy–enthalpy “compensation effect”. It is either used in chemical kinetics to account for activation enthalpies and entropies or in chemical thermodynamics to account for reaction enthalpies and reaction entropies. Both notions are quite spread, mostly in the biochemical literature. In its most precise form, it says that there is a linear relationship between ΔH and ΔS for changes in experimental variables, which is typically considered as an inherent property of complex biochemical systems. However—as explained in detail by a recent paper of Sharp [3]—“ S – H compensation... is insensitive to the details of the model, thus revealing little extra-thermodynamic or causal information about the system”.

According to this paper, the “compensation effect” typically works if ΔG is close to zero, compared to either ΔH or $T\Delta S$, which is trivial, as $\Delta G = \Delta H - T\Delta S$ holds. Thus, it reflects nothing more than this identity—which is based on the same close relation between G/T and S , as we can easily see by rearranging it to $\Delta(G/T) = \Delta(H/T) - \Delta S$.

References

1. William B, Jensen (2016) Vignettes in the history of chemistry. 1. What is the origin of the Gibbs–Helmholtz equation? Chem Texts. doi:[10.1007/s40828-015-0019-8](https://doi.org/10.1007/s40828-015-0019-8)
2. Roósz B, Visy CS, Nagypál I (2016) On the derivation of the Gibbs–Helmholtz equation. Chem Texts 2:5. doi:[10.1007/s40828-016-0023-7](https://doi.org/10.1007/s40828-016-0023-7)
3. Sharp K (2001) Entropy–enthalpy compensation: Fact or artefact? Protein Sci 10:661–667