

Helmholtz free energy

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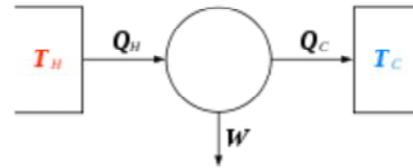
In thermodynamics, the **Helmholtz free energy** is a thermodynamic potential that measures the “useful” work obtainable from a closed thermodynamic system at a constant temperature and volume. For such a system, the negative of the difference in the Helmholtz energy is equal to the maximum amount of work extractable from a thermodynamic process in which temperature and volume are held constant. Under these conditions, it is minimized at equilibrium. The Helmholtz free energy was developed by Hermann von Helmholtz and is usually denoted by the letter *A* (from the German “Arbeit” or work), or the letter *F*. The IUPAC recommends the letter *A* as well as the use of name *Helmholtz energy*.^[1] In physics, the letter *F* is usually used to denote the Helmholtz energy, which is often referred to as the *Helmholtz function* or simply “free energy.”

While Gibbs free energy is most commonly used as a measure of thermodynamic potential, especially in the field of chemistry, the isobaric restriction on that quantity is inconvenient for some applications. For example, in explosives research, Helmholtz free energy is often used since explosive reactions by their nature induce pressure changes. It is also frequently used to define fundamental equations of state in accurate correlations of thermodynamic properties of pure substances.

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Thermodynamics



Branches

Classical · Statistical · Chemical
Equilibrium / Non-equilibrium
Thermofluids

Laws

Zeroth · First · Second · Third

Systems

State:

Equation of state
Ideal gas · Real gas
Phase of matter · Equilibrium
Control volume · Instruments

Processes:

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Adiabatic · Isentropic · Isenthalpic
Quasistatic · Polytropic
Free expansion
Reversibility · Irreversibility
Endoreversibility

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Thermal efficiency

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Property diagrams
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Temperature / Entropy (intro.) †
Pressure / Volume †
Chemical potential / Particle no. †
(† Conjugate variables)
Vapor quality
Reduced properties

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Definition

The Helmholtz energy is defined as:^[2]

$$A \equiv U - TS$$

where

- *A* is the Helmholtz free energy (SI: joules, CGS: ergs),
- *U* is the internal energy of the system (SI: joules, CGS: ergs),
- *T* is the absolute temperature (kelvins),
- *S* is the entropy (SI: joules per kelvin, CGS: ergs per kelvin).

The Helmholtz energy is the negative Legendre transform with respect to the entropy, *S*, of the fundamental relation in the energy representation, *U*(*S*, *V*, *N*). The natural variables of *A* are *T*, *V*, *N*.

Mathematical development

From the first law of thermodynamics we have

$$dU = \delta Q - \delta W,$$

where *U* is the internal energy, δQ is the energy added by heating and δW is the work done *by the system*. From the second law of thermodynamics, for a reversible process we may say that $\delta Q = TdS$. Also, in case of a reversible change, the work done can be expressed as $\delta W = pdV$

$$dU = TdS - pdV$$

Applying the product rule for differentiation to $d(TS) = TdS + SdT$, we have:

$$dU = d(TS) - SdT - pdV,$$

and:

$$d(U - TS) = -SdT - pdV$$

The definition of $A = U - TS$ enables to rewrite this as

$$dA = -SdT - pdV$$

Process functions:

Work · Heat

Material properties

$$\text{Specific heat capacity } c = \frac{T\partial S}{N\partial T}$$

$$\text{Compressibility } \beta = -\frac{1}{V}\frac{\partial V}{\partial p}$$

$$\text{Thermal expansion } \alpha = \frac{1}{V}\frac{\partial V}{\partial T}$$

Property database

Equations

Carnot's theorem

Clausius theorem

Fundamental relation

Ideal gas law

Maxwell relations

Table of thermodynamic equations

Potentials

Free energy · Free entropy

Internal energy $U(S,V)$

Enthalpy $H(S,p) = U + pV$

Helmholtz free energy $A(T,V) = U - TS$

Gibbs free energy $G(T,p) = H - TS$

History and culture

Philosophy:

Entropy and time · Entropy and life

Brownian ratchet

Maxwell's demon

Heat death paradox

Loschmidt's paradox

Synergetics

History:

General · Heat · Entropy · Gas laws

Perpetual motion

Theories:

Caloric theory · Vis viva

Theory of heat

Mechanical equivalent of heat

Motive power

Publications:

"An Experimental Enquiry Concerning ... Heat"

"On the Equilibrium of Heterogeneous Substances"

This relation is also valid for a process that is not reversible because A is a thermodynamic function of state.

Minimum free energy and maximum work principles

The laws of thermodynamics are only directly applicable to systems in thermal equilibrium. If we wish to describe phenomena like chemical reactions, then the best we can do is to consider suitably chosen initial and final states in which the system is in (metastable) thermal equilibrium. If the system is kept at fixed volume and is in contact with a heat bath at some constant temperature, then we can reason as follows.

Since the thermodynamical variables of the system are well defined in the initial state and the final state, the internal energy increase, ΔU , the entropy increase ΔS , and the work performed by the system, W , are well-defined quantities. Conservation of energy implies:

$$\Delta U_{\text{bath}} + \Delta U + W = 0$$

The volume of the system is kept constant. This means that the volume of the heat bath does not change either and we can conclude that the heat bath does not perform any work. This implies that the amount of heat that flows into the heat bath is given by:

$$Q_{\text{bath}} = \Delta U_{\text{bath}} = -(\Delta U + W)$$

The heat bath remains in thermal equilibrium at temperature T no matter what the system does. Therefore the entropy change of the heat bath is:

$$\Delta S_{\text{bath}} = \frac{Q_{\text{bath}}}{T} = -\frac{\Delta U + W}{T}$$

The total entropy change is thus given by:

$$\Delta S_{\text{bath}} + \Delta S = -\frac{\Delta U - T\Delta S + W}{T}$$

Since the system is in thermal equilibrium with the heat bath in the initial and the final states, T is also the temperature of the system in these states. The fact that the system's temperature does not change allows us to express the numerator as the free energy change of the system:

"Reflections on the Motive Power of Fire"

Timelines of:
Thermodynamics · Heat engines

Art:
Maxwell's thermodynamic surface

Education:
Entropy as energy dispersal

Scientists

Daniel Bernoulli
Sadi Carnot
Benoît Paul Émile Clapeyron
Rudolf Clausius
Hermann von Helmholtz
Constantin Carathéodory
Pierre Duhem
Josiah Willard Gibbs
James Prescott Joule
James Clerk Maxwell
Julius Robert von Mayer
William Rankine
John Smeaton
Georg Ernst Stahl
Benjamin Thompson
William Thomson, 1st Baron Kelvin
John James Waterston

$$\Delta S_{\text{bath}} + \Delta S = -\frac{\Delta A + W}{T}$$

Since the total change in entropy must always be larger or equal to zero, we obtain the inequality:

$$W \leq -\Delta A$$

If no work is extracted from the system then

$$\Delta A \leq 0$$

We see that for a system kept at constant temperature and volume, the total free energy during a spontaneous change can only decrease, that the total amount of work that can be extracted is limited by the free energy decrease, and that increasing the free energy requires work to be done on the system.

This result seems to contradict the equation $dA = -SdT - PdV$, as keeping T and V constant seems to imply $dA = 0$ and hence $A = \text{constant}$. In reality there is no contradiction. After the spontaneous change, the system, as described by thermodynamics, is a different system with a different free energy function than it was before the spontaneous change. Thus, we can say that $\Delta A = A_2 - A_1 \leq 0$ where the A_i are different thermodynamic functions of state.

One can imagine that the spontaneous change is carried out in a sequence of infinitesimally small steps. To describe such a system thermodynamically, one needs to enlarge the thermodynamical state space of the system. In case of a chemical reaction, one must specify the number of particles of each type. The differential of the free energy then generalizes to:

$$dA = -SdT - pdV + \sum_j \mu_j dN_j$$

where the N_j are the numbers of particles of type j and the μ_j are the corresponding chemical potentials. This equation is then again valid for both reversible and non-reversible changes. In case of a spontaneous change at constant T and V, the last term will thus be negative.

In case there are other external parameters the above equation generalizes to:

$$dA = -SdT - \sum_i X_i dx_i + \sum_j \mu_j dN_j$$

Here the x_i are the external variables and the X_i the corresponding generalized forces.

Relation to the partition function

A system kept at constant volume and temperature is described by the canonical ensemble. The probability to find the system in some energy eigenstate r is given by:

$$P_r = \frac{e^{-\beta E_r}}{Z}$$

where

$$\beta \equiv \frac{1}{kT}$$

E_r = energy of eigenstate r

$$Z = \sum_r e^{-\beta E_r}$$

Z is called the partition function of the system. The fact that the system does not have a unique energy means that the various thermodynamical quantities must be defined as expectation values. In the thermodynamical limit of infinite system size, the relative fluctuations in these averages will go to zero.

The average internal energy of the system is the expectation value of the energy and can be expressed in terms of Z as follows:

$$U \equiv \langle E \rangle = \sum_r P_r E_r = -\frac{\partial \log Z}{\partial \beta}$$

If the system is in state r , then the generalized force corresponding to an external variable x is given by

$$X_r = -\frac{\partial E_r}{\partial x}$$

The thermal average of this can be written as:

$$X = \sum_r P_r X_r = \frac{1}{\beta} \frac{\partial \log Z}{\partial x}$$

Suppose the system has one external variable x . Then changing the system's temperature parameter by $d\beta$ and the external variable by dx will lead to a change in $\log Z$:

$$d(\log Z) = \frac{\partial \log Z}{\partial \beta} d\beta + \frac{\partial \log Z}{\partial x} dx = -U d\beta + \beta X dx$$

If we write $U d\beta$ as:

$$U d\beta = d(\beta U) - \beta dU$$

we get:

$$d(\log Z) = -d(\beta U) + \beta dU + \beta X dx$$

This means that the change in the internal energy is given by:

$$dU = \frac{1}{\beta} d(\log Z + \beta U) - X dx$$

In the thermodynamic limit, the fundamental thermodynamic relation should hold:

$$dU = T dS - X dx$$

This then implies that the entropy of the system is given by:

$$S = k \ln Z + \frac{U}{T} + c$$

where c is some constant. The value of c can be determined by considering the limit $T \rightarrow 0$. In this limit the entropy becomes $S = k \log \Omega_0$ where Ω_0 is the ground state degeneracy. The partition function in this limit is $\Omega_0 e^{-\beta U_0}$ where U_0 is the ground state energy. Thus, we see that $c = 0$ and that:

$$A = -kT \ln(Z)$$

Bogoliubov inequality

Computing the free energy is an intractable problem for all but the simplest models in statistical physics. A powerful approximation method is mean field theory, which is a variational method based on the Bogoliubov inequality. This inequality can be formulated as follows.

Suppose we replace the real Hamiltonian H of the model by a trial Hamiltonian \tilde{H} , which has different interactions and may depend on extra parameters that are not present in the original model. If we choose this trial Hamiltonian such that

$$\langle \tilde{H} \rangle = \langle H \rangle$$

where both averages are taken with respect to the canonical distribution defined by the trial Hamiltonian \tilde{H} , then

$$A \leq \tilde{A}$$

where A is the free energy of the original Hamiltonian and \tilde{A} is the free energy of the trial Hamiltonian. By including a large number of parameters in the trial Hamiltonian and minimizing the free energy we can expect to get a close approximation to the exact free energy.

The Bogoliubov inequality is often formulated in a slightly different but equivalent way. If we write the Hamiltonian as:

$$H = H_0 + \Delta H$$

where H_0 is exactly solvable, then we can apply the above inequality by defining

$$\tilde{H} = H_0 + \langle \Delta H \rangle_0$$

Here we have defined $\langle X \rangle_0$ to be the average of X over the canonical ensemble defined by H_0 . Since \tilde{H} defined this way differs from H_0 by a constant, we have in general

$$\langle X \rangle_0 = \langle X \rangle$$

Therefore

$$\langle \tilde{H} \rangle = \langle H_0 + \langle \Delta H \rangle \rangle = \langle H \rangle$$

And thus the inequality

$$A \leq \tilde{A}$$

holds. The free energy \tilde{A} is the free energy of the model defined by H_0 plus $\langle \Delta H \rangle$. This means that

$$\tilde{A} = \langle H_0 \rangle_0 - TS_0 + \langle \Delta H \rangle_0 = \langle H \rangle_0 - TS_0$$

and thus:

$$A \leq \langle H \rangle_0 - TS_0$$

Proof

For a classical model we can prove the Bogoliubov inequality as follows. We denote the canonical probability distributions for the Hamiltonian and the trial Hamiltonian by P_r and \tilde{P}_r , respectively. The inequality:

$$\sum_r \tilde{P}_r \log(\tilde{P}_r) \geq \sum_r \tilde{P}_r \log(P_r)$$

then holds. To see this, consider the difference between the left hand side and the right hand side. We can write this as:

$$\sum_r \tilde{P}_r \log\left(\frac{\tilde{P}_r}{P_r}\right)$$

Since

$$\log(x) \geq 1 - \frac{1}{x}$$

it follows that:

$$\sum_r \tilde{P}_r \log\left(\frac{\tilde{P}_r}{P_r}\right) \geq \sum_r (\tilde{P}_r - P_r) = 0$$

where in the last step we have used that both probability distributions are normalized to 1.

We can write the inequality as:

$$\langle \log(\tilde{P}_r) \rangle \geq \langle \log(P_r) \rangle$$

where the averages are taken with respect to \tilde{P}_r . If we now substitute in here the expressions for the probability distributions:

$$P_r = \frac{\exp[-\beta H(r)]}{Z}$$

and

$$\tilde{P}_r = \frac{\exp[-\beta \tilde{H}(r)]}{\tilde{Z}}$$

we get:

$$\langle -\beta \tilde{H} - \log(\tilde{Z}) \rangle \geq \langle -\beta H - \log(Z) \rangle$$

Since the averages of H and \tilde{H} are, by assumption, identical we have:

$$A \leq \tilde{A}$$

Here we have used that the partition functions are constants with respect to taking averages and that the free energy is proportional to minus the logarithm of the partition function.

We can easily generalize this proof to the case of quantum mechanical models. We denote the eigenstates of \tilde{H} by $|r\rangle$. We denote the diagonal components of the density matrices for the canonical distributions for H and \tilde{H} in this basis as:

$$P_r = \left\langle r \left| \frac{\exp[-\beta H]}{Z} \right| r \right\rangle$$

and

$$\tilde{P}_r = \left\langle r \left| \frac{\exp[-\beta \tilde{H}]}{\tilde{Z}} \right| r \right\rangle = \frac{\exp(-\beta \tilde{E}_r)}{\tilde{Z}}$$

where the \tilde{E}_r are the eigenvalues of \tilde{H}

We assume again that the averages of H and \tilde{H} in the canonical ensemble defined by \tilde{H} are the same:

$$\langle \tilde{H} \rangle = \langle H \rangle$$

where

$$\langle H \rangle = \sum_r \tilde{P}_r \langle r | H | r \rangle$$

The inequality

$$\sum_r \tilde{P}_r \log(\tilde{P}_r) \geq \sum_r \tilde{P}_r \log(P_r)$$

still holds as both the P_r and the \tilde{P}_r sum to 1. On the l.h.s. we can replace:

$$\log(\tilde{P}_r) = -\beta\tilde{E}_r - \log(\tilde{Z})$$

On the right hand side we can use the inequality

$$\langle \exp(X) \rangle_r \geq \exp(\langle X \rangle_r)$$

where we have introduced the notation

$$\langle Y \rangle_r \equiv \langle r | Y | r \rangle$$

for the expectation value of the operator Y in the state r. See here for a proof. Taking the logarithm of this inequality gives:

$$\log[\langle \exp(X) \rangle_r] \geq \langle X \rangle_r$$

This allows us to write:

$$\log(P_r) = \log[\langle \exp(-\beta H - \log(Z)) \rangle_r] \geq \langle -\beta H - \log(Z) \rangle_r$$

The fact that the averages of H and \tilde{H} are the same then leads to the same conclusion as in the classical case:

$$A \leq \tilde{A}$$

Generalized Helmholtz energy

In the more general case, the mechanical term ($p dV$) must be replaced by the product of the volume times the stress times an infinitesimal strain:^[3]

$$dA = V \sum_{ij} \sigma_{ij} d\epsilon_{ij} - SdT + \sum_i \mu_i dN_i$$

where σ_{ij} is the stress tensor, and ϵ_{ij} is the strain tensor. In the case of linear elastic materials that obey Hooke's Law, the stress is related to the strain by:

$$\sigma_{ij} = C_{ijkl} \epsilon_{kl}$$

where we are now using Einstein notation for the tensors, in which repeated indices in a product are summed. We may integrate the expression for dA to obtain the Helmholtz energy:

$$\begin{aligned} A &= \frac{1}{2} V C_{ijkl} \epsilon_{ij} \epsilon_{kl} - ST + \sum_i \mu_i N_i \\ &= \frac{1}{2} V \sigma_{ij} \epsilon_{ij} - ST + \sum_i \mu_i N_i \end{aligned}$$

Application to fundamental equations of state

The Helmholtz free energy function for a pure substance (together with its partial derivatives) can be used to determine all other thermodynamic properties for the substance. See, for example, the equations of state for water, as given by the IAPWS in their IAPWS-95 (<http://www.iapws.org/relguide/IAPWS95-Rev.pdf>) release.

See also

- Gibbs free energy for thermodynamics history overview and discussion of *free energy*
- Grand potential
- Work content - for applications to chemistry
- Statistical mechanics
- This page details the Helmholtz energy from the point of view of thermal and statistical physics.
- Bennett acceptance ratio for an efficient way to calculate free energy differences, and comparison with other methods.

References

- [^] (<http://www.iupac.org/goldbook/H02772.pdf>) Gold Book. IUPAC. <http://www.iupac.org/goldbook/H02772.pdf>. Retrieved 2007-11-04.
- [^] Levine, Ira. N. (1978). "*Physical Chemistry*" McGraw Hill: University of Brooklyn
- [^] Landau, L. D.; Lifshitz, E. M. (1986) (in English). *Theory of Elasticity (Course of Theoretical Physics Volume 7)*. (Translated from Russian by J.B. Sykes and W.H. Reid) (Third ed. ed.). Boston, MA: Butterworth Heinemann. ISBN 0-7506-2633-X.

Further reading

- Atkins' *Physical Chemistry*, 7th edition, by Peter Atkins and Julio de Paula, Oxford University Press
- HyperPhysics Helmholtz Free Energy [1] (<http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/helmholtz.html>)

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Categories: Fundamental physics concepts | State functions | Thermodynamic free energy

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