Thermodynamic potentials

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1. The laws[1] of thermodynamics

Thermodynamics is the science of heat transfer. Usually, we are talking about equilibrium thermodynamics, meaning that changes in the observed system are slow and continuous. There are four laws, usually given in the following order.

1. The energy of the universe does not change; it is always conserved.
2. In a physical process, the entropy of the world always increases.
3. The entropy of a system at a temperature of absolute zero[2] is zero.

The last one is the zeroth:

- If A is a system in thermal equilibrium with the system B, and B is in thermal equilibrium with the system C, then the systems A and C are also in thermal equilibrium.

2. Basics

Thermodynamics is the general branch of physics which describes static states of macroscopic systems. By “static”, we mean equilibrium states. It is mainly concerned with forms of energy, especially heat, but then what branch of physics is not? The word heat indicates a transfer of energy, not just energy *per se*. Only differences of energy are measured, and for any state, its internal energy U is defined relative to some standard or base state, a fiducial state,

Ignoring electromagnetic or atomic or nuclear effects, the internal energy of a system can be written as

$$U(V, N_1, N_2, \ldots) \qquad (1)$$

where V is its volume and the N_i are the mole numbers of its constituent chemical components. All these parameters, including the energy U, are ***extensive parameters***, meaning that if two subsystems are combined, the resultant parameters are the sums of those of the subsystems.

The energy of a system can be increased mechanically or by adding heat energy.

$$dU = dQ + dW_M \qquad (2)$$

with $$dW_M = -PdV \qquad (3)$$

where P is the pressure and V is the volume of the system, defined such that that work on the system increases its energy.

We then define the ***entropy*** S of a system as an extensive parameter defined for equilibrium states. “The values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.”[3] So S must be added to the equation of state.

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[1] In English, on always refers to these as laws – physical laws – whereas the French, always alert to a nuance, refer to them as *principes*.

[2] Absolute zero is 0 Kelvin, or -273.15° Celsius.

[3] Callan, 27.

$U = U(S, V, N_1, \dots N_r)$. (4)

An equilibrium state is then described by one of several principles. The entropy is defined to vanish at absolute zero:

$$\left(\frac{\partial U}{\partial S}\right)_{V,N_1,\dots,N_r} = 0 \qquad (5)$$

The following intensive (non-addable) parameters are then defined:

$$\left(\frac{\partial U}{\partial S}\right)_{V,N_1,\dots,N_r} := T \qquad 6$$

$$-\left(\frac{\partial U}{\partial V}\right)_{S,N_1,\dots,N_r} := P \qquad (7)$$

$$\left(\frac{\partial U}{\partial N_j}\right)_{V,N_1,\dots,N_k,\dots} := \mu_j \qquad (8)$$

where T is the temperature, P the pressure and μ_j the chemical potential of the j^{th} component.

From Callan, we have two equivalent principles of thermodynamics:.

1. **Entropy maximum principle**. The equilibrium value of any unconstrained internal parameter is such as to maximize the entropy for the given value of the total internal energy.
2. **Energy minimum principle**. The equilibrium value of any unconstrained internal parameter is such as to minimize the energy for the given value of the total entropy.[4]

These two principles can be shown to be equivalent.

The basic formula for the internal energy U as a function ofentropy S, temperature T, pressure p and volume V (and the chemical potentials, N_i) is

$U = TS - pV + \mu N$

where μN stands for the sum over different chemical potentials

$$\sum_i \mu_i N_i$$

representing the quasi-static chemical work and

$dU = TdS - pdV + \mu dN$

The term -pdV is the work done on the system by a volume change; its sign is chosen so as to be positive if the energy of the system is increased.

Experimental conditions vary. They may occur, like most chemical experiments, at constant (atmospheric) pressure. Others may be restricted to a container at constant volume or may be in contact with heat sinks and sources to maintain constant temperature. Depending on the problem at hand, It may be simpler to solve for the equilibrium state if the formula had different independent variables. That is what Legendre transformations do.

3. Legendre transformations

Given a formula

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[4] Callan, 133.

Y = Y(X)

then

$$P = \frac{\partial Y}{\partial X}$$

is the slope of the curve at a given point. We would like an equivalent representation of the system but one where the independent variable is P rather than X. In order to do this, we will use the X-intercept ψ of the Y axis of a tangent of constant slope at X. Then the curve may be represented by the set of slopes and intercepts just as well as by the formula Y(X).

The slope is given by

$$P = \frac{Y - \psi}{X - 0}$$

which can be arranged to give the **Legendre transformation**

ψ = Y – PX

Then

dψ = dY – PdX – XdP = -XdP

or, since dY = PdX,

$$-X = \frac{d\psi}{dP}$$

so the inverse transformation is just

Y = XP + ψ.

In general, for

Y = Y(X_o,X_2,…,X_i)

the partial slope of this hypersurface is given by

$$P_k = \frac{\partial Y}{\partial X_k}$$

and the Legendre transformation is

$$\psi = Y - \sum_k P_k X_k$$

Example from Callan, problem 5.2-1:

$$y = \frac{x^2}{10} \qquad \text{gives} \qquad P = \frac{\partial Y}{\partial X} = \frac{x}{5}$$

so eliminating x in terms of P gives

$$\psi(P) = y - Px = -\frac{5}{2}P^2$$

Inversely,

$$-X = \frac{\partial \psi}{\partial P} = -5P$$

so

$$Y(X) = \psi + XP = \frac{X^2}{10}$$

as it must.

4. Principle thermodynamic potentials

The most used thermodynamic potentials are indicated in the following table and are all Legendre transforms of the internal energy U as shown.

We can identify each term with a type of energy:

- TS with heat energy,
- pV with work done on the system, due to volume-change energy (as when a piston is pushed) and
- the sum $\sum_i \mu_i N_i$ as the energy of chemical bonding.

We will ignore such things as electromagnetic or atomic energy.

Name	Symbol	Formula	Natural variables	Variable change	Physical interpretation (infinitesimal, quasi-equilibrium changes)
Internal energy	U	$TS - pV + \sum_i \mu_i N_i$	S, V, $\{N_i\}$	-	Total internal energy of system
Helmholtz free energy	F (or A)	U – TS	T, V, $\{N_i\}$	S → T	Max useable energy at constant T & V after system pays “entropy tax”
Enthalpy	H	U + pV	S, p, $\{N_i\}$	V → P	Total heat energy available in system at constant P after V change
Gibbs free energy	G	U + pV – TS	T, p, $\{N_i\}$	S → T and V → P	Max energy available at constant T & P after V change and “S tax”

The above-cited energy-minimum principle applies to all these potentials under specific circumstances.

> **Helmholtz Potential Minimum Principle**. “The equilibrium value of any unconstrained internal parameter in a system in diathermal contact with a heat reservoir minimizes the Helmholtz potential over the manifold of states for which $T = T^r$ [at constant T].”[5]
>
> **Enthalpy Minimum Principle**. “The equilibrium value of any unconstrained internal parameter in a system in contact with a pressure reservoir minimizes the enthalpy over the manifold of states of constant pressure (equal to that of the pressure reservoir).”[6]
>
> **Gibbs Potential Minimum Principle**. “The equilibrium value of any unconstrained internal parameter in a system in contact with a thermal and a pressure reservoir minimizes the Gibbs potential at constant temperature and pressure (equal to those of the respective reservoirs).”[7]

We can attribute physical meanings to these potentials.

In the case of ***enthalpy***, a system at constant P can expand or contract, therefore losing energy to move around molecules. This volume-change energy is exactly what is subtracted from U in order to derive H. So enthalpy is the energy released as heat by the system at constant P. Or, in the other direction,

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[5] Callan, 155.

[6] Callan, 156.

[7] This and the following definitions are all from Callan, 157, 161, 159, 167.

> ...heat added to a system at constant pressure and at constant values of all the remaining extensive parameters (other than S and V) appears as an increase in the enthalpy.

As for the Helmholtz free energy,

> … the work delivered in a reversible process, by a system in contact with a thermal reservoir [so at constant T], is equal to the decrease in the Helmholtz potential of the system.

The Helmholtz free energy is thus the available work at constant temperature and volume. The term TS represents the “entropy tax” which the system must pay in order for the total entropy of the universe to remain zero.

The Gibbs free energy is useful when T and P are constant, which is the usual case of chemical reactions open to the atmosphere, which acts as a reservoir of T and P. Gibbs free energy is thus much beloved of chemists. As Callan points out, it may also be true “… in a small subsystem of a larger system that acts as both a thermal and a pressure reservoir (as in the fermentation of a grape in a large wine vat).”

5. Spontaneous reactions

Suppose there is only one thermodynamic system in the universe and that its T and V are constant. Then the sum of the entropy changes of the system and of its surroundings is the entropy change of the universe.

$$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys} \tag{9}$$

If the energy of the system changes by an amount ΔU, then the surroundings will change by -ΔU, and

$$\Delta S_{surr} = \frac{-\Delta U}{T}$$

so

$$\Delta S_{univ} = \Delta S_{sys} - \frac{-\Delta U}{T}$$

which means

$$\Delta U_{univ} = T\Delta S U_{univ} = -(\Delta U - T\Delta S) = -\Delta F$$

So the entropy maximum principle says that for constant T and V, the change in the Helmholtz free energy must be negative, so that $\Delta S_{univ} = \frac{\Delta U_{univ}}{T}$ > 0.

Similarly, if only a spontaneous chemical reaction occurs at constant T and P, then a change in heat energy (enthalpy) of the system means the surroundings change by the negative of that., i.e.,$-\Delta H_{sys}$. So equation (1) gives

$$\Delta S_{univ} = -\frac{-\Delta H_{sys}}{T} + \Delta S_{sys}$$

The only change in the universe is due to the dispersal of energy in a quantity we may call $-\Delta G$. Therefore

$$\Delta S_{univ} = -\frac{\Delta G}{T} = -\frac{-\Delta H_{sys}}{T} + \Delta S_{sys}$$

which may be rewritten as

$$\Delta G = \Delta H_{sys} - T\Delta S_{sys}$$

which is the Gibbs free energy.

6. Note on entropy

Entropy is generally stated to be related to the number of states available to a system in statistical mechanics by the Boltzmann entropy formula S = k ln(W), where k is the Boltzmann constant and W (for "Warscheinlichkiet") is the probability of the system, essentially the number of indistinguishable arrangements of its molecules. This model only seems to work when chemical reactions do not take place. Consider adding these two types of molecules:

$2H_{2} + O_{2} \rightarrow \quad 2H_{2}O$ + lots of energy.

The final molecules display less randomness than the first. So a better definition is Lambert's:

> "*Entropy change is the measure of how more widely a specific quantity of molecular energy is dispersed in a process, whether isothermal gas expansion, gas or liquid mixing, reversible heating and phase change or chemical reactions, as shown by the Gibbs free energy equation/T*." (The last means G/T.)[8]

This definition goes along with his statement of the second law as:

> "*Energy of all types changes from being localized to becoming more spread out, dispersed in space if that energy is not constrained from doing so.*"

For more on this subject, see Lambert's web site.

7. Bibliography

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[8] Entropy sites, a guide. http://entropysite.oxy.edu/#intro.