

15.1: Differential Forms of Fundamental Equations

The fundamental thermodynamic equations follow from five primary thermodynamic definitions and describe internal energy, enthalpy, Helmholtz energy, and Gibbs energy in terms of their natural variables. Here they will be presented in their differential forms.

Introduction

The fundamental thermodynamic equations describe the thermodynamic quantities U , H , G , and A in terms of their natural variables. The term "natural variable" simply denotes a variable that is one of the convenient variables to describe U , H , G , or A . When considered as a whole, the four fundamental equations demonstrate how four important thermodynamic quantities depend on variables that can be controlled and measured experimentally. Thus, they are essentially equations of state, and using the fundamental equations, experimental data can be used to determine sought-after quantities like G or H .

First Law of Thermodynamics

The first law of thermodynamics is represented below in its differential form

$$dU = dq + dw \quad (15.1.1)$$

where

- U is the internal energy of the system,
- q is heat flow of the system, and
- w is the work of the system.

Recall that U is a state function, while q and w are path functions. The first law states that internal energy changes occur only as a result of heat flow and work done.

It is assumed that w refers only to PV work, where

$$w = - \int P dV \quad (15.1.2)$$

The Principle of Clausius

The *Principle of Clausius* states that the entropy change of a system is equal to the ratio of heat flow in a reversible process to the temperature at which the process occurs. Mathematically this is written as

$$dS = \frac{dq_{rev}}{T} \quad (15.1.3)$$

where

- S is the entropy of the system,
- q_{rev} is the heat flow of a reversible process, and
- T is the temperature in Kelvin.

Internal Energy

The fundamental thermodynamic equation for internal energy follows directly from the first law and the principle of Clausius:

$$dU = dq + dw \quad (15.1.4)$$

$$dS = \frac{dq_{rev}}{T} \quad (15.1.5)$$

we have

$$dU = TdS + dw \quad (15.1.6)$$

Since only PV work is performed,

$$dU = TdS - PdV \quad (15.1.7)$$

The above equation is the fundamental equation for U with natural variables of entropy S and volume V .

Enthalpy

Mathematically, enthalpy is defined as

$$H = U + PV \quad (15.1.8)$$

where H is enthalpy of the system, p is pressure, and V is volume. The fundamental thermodynamic equation for enthalpy follows directly from its definition (Equation 15.1.8) and the fundamental equation for internal energy (Equation 15.1.7) :

$$dH = dU + d(PV) \quad (15.1.9)$$

$$dH = dU + PdV + VdP \quad (15.1.10)$$

Because $dU = TdS - PdV$, the enthalpy equation becomes:

$$dH = TdS - PdV + PdV + VdP \quad (15.1.11)$$

$$dH = TdS + VdP \quad (15.1.12)$$

The above equation is the fundamental equation for H . The natural variables of enthalpy are S and P , entropy and pressure.

Gibbs Energy

The mathematical description of Gibbs energy is as follows

$$G = U + PV - TS = H - TS \quad (15.1.13)$$

where G is the Gibbs energy of the system. The fundamental thermodynamic equation for Gibbs Energy follows directly from its definition 15.1.13 and the fundamental equation for enthalpy 15.1.8

$$dG = dH - d(TS) \quad (15.1.14)$$

$$dG = dH - TdS - SdT \quad (15.1.15)$$

Since $dH = TdS + VdP$,

$$dG = TdS + VdP - TdS - SdT \quad (15.1.16)$$

$$dG = VdP - SdT \quad (15.1.17)$$

The above equation is the fundamental equation for G . The natural variables of Gibbs energy are P and T , pressure and temperature.

Helmholtz Energy

Mathematically, Helmholtz energy is defined as

$$A = U - TS \quad (15.1.18)$$

where A is the Helmholtz energy of the system, which sometimes also written as the symbol F . The fundamental thermodynamic equation for Helmholtz energy follows directly from its definition (Equation 15.1.18) and the fundamental equation for internal energy (Equation 15.1.7):

$$dA = dU - d(TS) \quad (15.1.19)$$

$$dA = dU - TdS - SdT \quad (15.1.20)$$

Since $dU = TdS - PdV$,

$$dA = TdS - PdV - TdS - SdT \quad (15.1.21)$$

$$dA = -PdV - SdT \quad (15.1.22)$$

The above equation is the fundamental equation for A with natural variables of V and T .

Importance/Relevance of Fundamental Equations

The differential fundamental equations describe U, H, G, and A in terms of their natural variables. The natural variables become useful in understanding not only how thermodynamic quantities are related to each other, but also in analyzing relationships between measurable quantities (i.e. P, V, T) in order to learn about the thermodynamics of a system. Below is a table summarizing the natural variables for U, H, G, and A:

Thermodynamic Quantity	Natural Variables
U (internal energy)	S, V
H (enthalpy)	S, P
G (Gibbs energy)	T, P
A (Helmholtz energy)	T, V

For these definitions to hold, it is assumed that **only** PV work is done and that **only reversible** processes are used. These assumptions are required for the first law and the principle of Clausius to remain valid. Also, these equations do not account include n , the number of moles, as a variable. When n is included, the equations appear different, but the essence of their meaning is captured without including the n -dependence.

References

1. DOI: 10.1063/1.1749582
2. DOI: 10.1063/1.1749549
3. DOI:10.1103/PhysRev.3.273
4. *A Treatise on Physical Chemistry*, 3rd ed.; Taylor, H. S. and Glasstone, S., Eds.; D. Van Nostrand Company: New York, 1942; Vol. 1; p 454-485.

Problems

1. If the assumptions made in the derivations above were not made, what would effect would that have? Try to think of examples were these assumptions would be violated. Could the definitions, principles, and laws used to derive the fundamental equations still be used? Why or why not?
2. For what kind of system does the number of moles not change? This said, do the fundamental equations without n -dependence apply to a wide range of processes and systems?
3. Derive the Maxwell Relations.
4. Derive the expression

$$\left(\frac{\partial H}{\partial P}\right)_{T,n} = -T\left(\frac{\partial V}{\partial T}\right)_{P,n} + V \quad (15.1.23)$$

Then apply this equation to an ideal gas. Does the result seem reasonable?

5. Using the definition of Gibbs energy and the conditions observed at phase equilibria, derive the Clapeyron equation.

Answers

1. If it was not assumed that PV-work was the only work done, then the work term in the second law of thermodynamics equation would include other terms (e.g. for electrical work, mechanical work). If reversible processes were not assumed, the Principle of Clausius could not be used. One example of such situations could be the movement of charged particles towards a region of like charge (electrical work) or an irreversible process like combustion of hydrocarbons or friction.
2. In general, a closed system of non-reacting components would fit this description. For example, the number of moles would not change for a closed system in which a gas is sealed (to prevent leaks) in a container and allowed to expand/contract.
3. See the Maxwell Relations section.
4. $\left(\frac{\partial H}{\partial P}\right)_{T,n} = 0$ for an ideal gas. Since there are no interactions between ideal gas molecules, changing the pressure will not involve the formation or breaking of any intermolecular interactions or bonds.

5. See the third outside link.

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