# Chapter 5 — Thermodynamic Functions

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# 1 Thermodynamic Functions

The complete description of a thermodynamic system requires the choice of a set of state variables and the construction of state functions called thermodynamic potentials. These functions make it possible to determine the equilibrium state and the stability of the system, and to calculate physical quantities (heat capacities, compressibility, expansion coefficient, etc.).

## 1.1 Choice of Thermodynamic Variables

### 1.1.1 Extensive and Intensive Variables

State variables fall into two categories:

- **Extensive variables**: proportional to the size of the system. They add up when two subsystems are combined.
  - Internal energy $U$ (J)
  - Volume $V$ ($m^3$)
  - Number of moles $n$ or number of particles $N$
  - Entropy $S$ ($J \cdot K^{-1}$)
  - Enthalpy $H$ (J)
  - Free energy $F$ (J)
  - Free enthalpy $G$ (J)
- **Intensive variables**: independent of the size of the system. They take the same value in two subsystems at equilibrium.
  - Temperature $T$ (K)
  - Pressure $P$ (Pa)
  - Chemical potential $\mu$ ($J \cdot mol^{-1}$)
  - Density $n/V$

### 1.1.2 Equation of State and Natural Variables

An equation of state relates the intensive and extensive variables. For a simple fluid, it is written in the form:

$$f(P, V, T, n) = 0 \qquad (1.1) \tag{1}$$

For example, for an ideal gas: $PV = nRT$.

Each thermodynamic potential has natural variables, that is, a set of variables whose knowledge is sufficient to determine all other properties of the system.

Table 1: Natural variables of the main potentials

| **Potential** | **Notation** | **Natural variables** |
|---|---|---|
| Internal energy | $U$ | $S$, $V$, $N$ |
| Enthalpy | $H$ | $S$, $P$, $N$ |
| Helmholtz free energy | $F$ | $T$, $V$, $N$ |
| Gibbs free enthalpy | $G$ | $T$, $P$, $N$ |
| Grand potential | $\Omega$ | $T$, $V$, $\mu$ |

## 1.2 Thermodynamic Potentials

### 1.2.1 Fundamental Relation and Internal Energy

The fundamental postulate of thermodynamics states that all information about a system is contained in a characteristic function. The most fundamental is the internal energy $U(S, V, N)$, whose differential is written:

$$dU = TdS - PdV + \mu dN \qquad (1.2) \tag{2}$$

This relation, called the Gibbs relation, is the exact total differential of $U$. From it, we deduce the thermodynamic identities:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \tag{1.3}$$

$$-P = \left(\frac{\partial U}{\partial V}\right)_{S,N} \tag{1.4}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{1.5}$$

### 1.2.2 Legendre Transformations

The other thermodynamic potentials are obtained from $U$ by Legendre transformations, which consist in replacing an extensive variable by its conjugate intensive variable.

**Enthalpy** $H(S, P, N)$
We replace $V$ by $P$:

$$H = U + PV \qquad (1.6) \tag{3}$$

hence:

$$dH = TdS + VdP + \mu dN \qquad (1.7) \tag{4}$$

**Helmholtz Free Energy** $F(T, V, N)$
We replace $S$ by $T$:

$$F = U - TS \qquad (1.8) \tag{5}$$

hence:

$$dF = -SdT - PdV + \mu dN \qquad (1.9) \tag{6}$$

**Gibbs Free Enthalpy** $G(T, P, N)$
We simultaneously replace $S$ by $T$ and $V$ by $P$:

$$G = U - TS + PV = H - TS = F + PV \qquad (1.10) \tag{7}$$

hence:

$$dG = -SdT + VdP + \mu dN \qquad (1.11) \tag{8}$$

**Grand Potential** $\Omega(T, V, \mu)$
We replace $S$ by $T$ and $N$ by $\mu$:

$$\Omega = U - TS - \mu N = F - \mu N = -PV \qquad (1.12) \tag{9}$$

hence:

$$d\Omega = -SdT - PdV - Nd\mu \qquad (1.13) \tag{10}$$

### 1.2.3 Summary of Thermodynamic Potentials

**Maxwell Relations**

From each potential, the equality of cross derivatives provides Maxwell relations. For example, from $dF = -SdT - PdV$:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

These relations are very useful for expressing non-measurable quantities in terms of quantities accessible to experiment.

### 1.2.4 Physical Meaning of the Potentials

- **Internal energy** $U$: total energy of the system (microscopic). It is minimal at equilibrium for an isolated system ($S$, $V$, $N$ fixed).
- **Enthalpy** $H$: useful for transformations at constant pressure (chemical reactions in open air). $Q_P = \Delta H$.
- **Free energy** $F$: represents the maximum work extractable at constant temperature. It is minimal at equilibrium for a system at fixed $T$, $V$, $N$.
- **Free enthalpy** $G$: represents the maximum useful work at constant $T$ and $P$. It is minimal at equilibrium for a system at fixed $T$, $P$, $N$.
- **Grand potential** $\Omega$: useful in statistical physics, for open systems (particle exchange with a reservoir).

## 1.3 Heat Capacities

### 1.3.1 Definitions

Heat capacities measure the amount of heat required to raise the temperature of a system by one kelvin. A distinction is made between:

- **Heat capacity at constant volume**:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \qquad (1.14) \tag{11}$$

  It is related to the variation of internal energy at constant volume: $C_V = \left(\frac{\delta Q}{\delta T}\right)_V$.

- **Heat capacity at constant pressure**:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P \qquad (1.15) \tag{12}$$

  It is related to the variation of enthalpy at constant pressure: $C_P = \left(\frac{\delta Q}{\delta T}\right)_P$.

### 1.3.2 Mayer's Relation

Using the relation $H = U + PV$, it can be shown that:

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P \qquad (1.16) \tag{13}$$

For an ideal gas, $U$ depends only on $T$, so $\left(\frac{\partial U}{\partial V}\right)_T = 0$, and $PV = nRT$ gives $\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$. We then recover Mayer's relation:

$$C_P - C_V = nR \qquad (1.17) \tag{14}$$

### 1.3.3 Coefficient $\gamma$ and Molar Heat Capacities

The ratio of heat capacities is defined as:

$$\gamma = \frac{C_P}{C_V} \qquad (1.18) \tag{15}$$

For a monatomic ideal gas, $\gamma = 5/3 \approx 1.67$; for a diatomic gas, $\gamma = 7/5 = 1.4$.

Table 2: Molar heat capacities of some ideal gases

| **Gas** | $\boldsymbol{C_V}$ **(J·mol$^{-1}$·K$^{-1}$)** | $\boldsymbol{C_P}$ **(J·mol$^{-1}$·K$^{-1}$)** | $\boldsymbol{\gamma}$ |
|---|---|---|---|
| Monatomic (He, Ar) | $3/2\,R$ | $5/2\,R$ | 5/3 |
| Diatomic ($H_2$, $O_2$) | $5/2\,R$ | $7/2\,R$ | 7/5 |
| Polyatomic ($CO_2$, $CH_4$) | $3R$ | $4R$ | 4/3 |

### 1.3.4 Heat Capacities and Entropy

For an ideal gas, the entropy variation between two states is written:

$$\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right) \qquad (1.19) \tag{16}$$

or, in $(T, P)$ variables:

$$\Delta S = nC_P \ln\left(\frac{T_2}{T_1}\right) - nR\ln\left(\frac{P_2}{P_1}\right) \qquad (1.20) \tag{17}$$

## 1.4 Gibbs-Duhem Relation

### 1.4.1 Euler Equation and Extensivity

Internal energy is an extensive function: if all extensive variables are multiplied by a factor $\lambda$, then $U$ is also multiplied by $\lambda$:

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N) \qquad (1.21) \tag{18}$$

Differentiating with respect to $\lambda$ and setting $\lambda = 1$, we obtain Euler's theorem for homogeneous functions of degree 1:

$$U = TS - PV + \mu N \qquad (1.22) \tag{19}$$

This relation is called the Euler equation.

### 1.4.2 Derivation of the Gibbs-Duhem Relation

Differentiating the Euler equation:

$$dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu \qquad (1.23) \tag{20}$$

Comparing with the differential of $U$:

$$dU = TdS - PdV + \mu dN \qquad (1.24) \tag{21}$$

we obtain by subtraction:

$$SdT - VdP + Nd\mu = 0 \qquad (1.25) \tag{22}$$

### 1.4.3 Interpretation and Consequences

The Gibbs-Duhem relation shows that the three intensive variables $T$, $P$, and $\mu$ are not independent: knowing two of them determines the third.

At constant temperature ($dT = 0$): $d\mu = v\, dP$, where $v$ is the molar volume.

At constant pressure ($dP = 0$): $d\mu = -s\, dT$, where $s$ is the molar entropy.

For a single-component system: $\mu = g(T, P)$ (molar free enthalpy), which is consistent with $dG = -SdT + VdP + \mu dN$.

### 1.4.4 Application to Phase Equilibrium

At equilibrium between two phases $\alpha$ and $\beta$ of a pure substance, we have $T^\alpha = T^\beta$, $P^\alpha = P^\beta$, and $\mu^\alpha = \mu^\beta$. Applying the Gibbs-Duhem relation to each phase and subtracting:

$$(s^\beta - s^\alpha)dT - (v^\beta - v^\alpha)dP = 0 \qquad (1.26) \tag{23}$$

We recover the Clausius-Clapeyron equation:

$$\frac{dP}{dT} = \frac{s^\beta - s^\alpha}{v^\beta - v^\alpha} = \frac{L}{T\Delta v} \qquad (1.27) \tag{24}$$

where $L = T(s^\beta - s^\alpha)$ is the latent heat of transition.

### 1.4.5 Application to Mixtures

For a mixture of $k$ constituents, the Gibbs-Duhem relation generalizes to:

$$SdT - VdP + \sum_{i=1}^{k} N_i d\mu_i = 0 \qquad (1.28) \tag{25}$$

This relation is fundamental for the study of chemical equilibria and solutions.

## Chapter Summary

Table 3: Summary of key concepts of Chapter 5

| **Concept** | **Essential idea** |
|---|---|
| Extensive variables | Proportional to size ($U$, $V$, $S$, $N$). |
| Intensive variables | Independent of size ($T$, $P$, $\mu$). |
| Natural variables | Minimal set determining the potential ($U(S,V,N)$, $G(T,P,N)\dots$). |
| Legendre transformation | Changes an extensive variable into its conjugate intensive one. |
| $U$ | $dU = TdS - PdV + \mu dN$; minimal at fixed $S$, $V$, $N$. |
| $H = U + PV$ | $dH = TdS + VdP + \mu dN$; $Q_P = \Delta H$. |
| $F = U - TS$ | $dF = -SdT - PdV + \mu dN$; max work at constant $T$. |
| $G = U - TS + PV$ | $dG = -SdT + VdP + \mu dN$; max useful work at $T$, $P$. |
| $\Omega = -PV$ | Grand potential, useful for open systems. |
| Heat capacity $C_V$ | $C_V = (\partial U/\partial T)_V$. |
| Heat capacity $C_P$ | $C_P = (\partial H/\partial T)_P$. |
| Mayer's relation | $C_P - C_V = nR$ (ideal gas). |
| Gibbs-Duhem relation | $SdT - VdP + Nd\mu = 0$ (intensive variables not independent). |
| Clausius-Clapeyron | $\frac{dP}{dT} = \frac{L}{T\Delta v}$ (phase equilibrium). |