

4.3 Thermodynamic Functions

Four important and useful thermodynamic functions will be considered in this section (two of them have been encountered in the previous sections). These are the **internal energy** U , the **enthalpy** H , the **Helmholtz free energy** (or simply the **free energy**) Ψ and the **Gibbs free energy** (or simply the **Gibbs function**) G . These functions will be defined and examined below for both reversible and irreversible processes.

4.3.1 Reversible Processes

Consider first a reversible process.

The Internal Energy

The internal energy is

$$\begin{aligned} dU &= \delta W + \delta Q \\ &= -pdV + \theta dS \end{aligned} \quad (4.3.1)$$

the second line being valid for quasi-static processes. The properties of a pure compressible substance include V , θ , S and p . From 4.3.1, it is natural to take V and S as the state variables:

$$dU = \left(\frac{\partial U}{\partial V} \right)_S dV + \left(\frac{\partial U}{\partial S} \right)_V dS \quad (4.3.2)$$

so that

$$p = - \left(\frac{\partial U}{\partial V} \right)_S, \quad \theta = \left(\frac{\partial U}{\partial S} \right)_V \quad (4.3.3)$$

Thus $U(V, S)$ contains all the thermodynamic information about the system; given V and S one has an expression for U and can evaluate p and θ through differentiation. U is a **thermodynamic potential**, meaning that it provides information through a differentiation.

V and S are said to be the **canonical (natural) state variables** for U . By contrast, expressing the internal energy as a function of the volume and temperature, for example, $U = U(V, \theta)$, is not so useful, since this cannot provide all the necessary information regarding the state of the material. A new state function will be introduced below which has V and θ as canonical state variables.

Similarly, the equation of state $\theta(V, p)$ does not contain all the thermodynamic information. For example, there is no information about U or S , and this equation of state must be supplemented by another, just as the ideal gas law is supplemented by the caloric equation of state $U = U(\theta)$.

Returning to the internal energy function, and taking the differential relations between p , θ and U , Eqns. 4.3.3, and differentiating them again, and using the fact that $\partial^2 U / \partial V \partial S = \partial^2 U / \partial S \partial V$, one arrives at the **Maxwell relation**,

$$-\left(\frac{\partial p}{\partial S}\right)_V = \left(\frac{\partial \theta}{\partial V}\right)_S \quad (4.3.4)$$

The Helmholtz Free Energy

Define the (**Helmholtz**) free energy function through

$$\Psi = U - \theta S \quad (4.3.5)$$

One has

$$\begin{aligned} d\Psi &= dU - \theta dS - S d\theta \\ &= dU - \delta Q - S d\theta, \\ &= -pdV - S d\theta \end{aligned} \quad (4.3.6)$$

the second line being valid for reversible processes. Now V and θ have emerged as the natural state variables. Writing $\Psi = \Psi(V, \theta)$,

$$d\Psi = \left(\frac{\partial \Psi}{\partial V}\right)_\theta dV + \left(\frac{\partial \Psi}{\partial \theta}\right)_V d\theta \quad (4.3.7)$$

so that

$$p = -\left(\frac{\partial \Psi}{\partial V}\right)_\theta, \quad S = -\left(\frac{\partial \Psi}{\partial \theta}\right)_V \quad (4.3.8)$$

The Enthalpy and Gibbs Free Energy

The enthalpy is defined by Eqn. 4.1.18,

$$H = U + pV \quad (4.3.9)$$

To determine the canonical state variables, evaluate the increment:

$$\begin{aligned} dH &= dU + pdV + Vdp \\ &= \delta W + \delta Q + pdV + Vdp \end{aligned} \quad (4.3.10)$$

and so

$$dH = \theta dS + V dp \quad (4.3.11)$$

and the natural variables are p and S . Finally, the Gibbs free energy function is defined by

$$G = U - \theta S + pV \quad (4.3.12)$$

and the canonical state variables are p and θ .

The definitions, canonical state variables and Maxwell relations for all four functions are summarised in Table 4.3.1 below.

Thermo-dynamic potential	Symbol and appropriate variables	Definition	Differential relationship	Maxwell relation
Internal energy	$U(S, V)$		$dU = -pdV + \theta dS$	$\theta = \left(\frac{\partial U}{\partial S}\right)_V, p = -\left(\frac{\partial U}{\partial V}\right)_S$ $\left(\frac{\partial \theta}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
Enthalpy	$H(S, p)$	$H = U + pV$	$dH = Vdp + \theta dS$	$\theta = \left(\frac{\partial H}{\partial S}\right)_p, V = \left(\frac{\partial H}{\partial p}\right)_S$ $\left(\frac{\partial \theta}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
Helmholtz free energy	$\Psi(\theta, V)$	$\Psi = U - \theta S$	$d\Psi = -pdV - Sd\theta$	$S = -\left(\frac{\partial \Psi}{\partial \theta}\right)_V, p = -\left(\frac{\partial \Psi}{\partial V}\right)_\theta$ $\left(\frac{\partial S}{\partial V}\right)_\theta = \left(\frac{\partial p}{\partial \theta}\right)_V$
Gibbs free energy	$G(\theta, p)$	$G = U - \theta S + pV$	$dG = Vdp - Sd\theta$	$S = -\left(\frac{\partial G}{\partial \theta}\right)_p, V = \left(\frac{\partial G}{\partial p}\right)_\theta$ $\left(\frac{\partial S}{\partial p}\right)_\theta = -\left(\frac{\partial V}{\partial \theta}\right)_p$

Table 4.3.1: Thermodynamic Potential Functions and Maxwell relations

Mechanical variables: whereas the internal energy and the Helmholtz free energy are functions of a kinematic variable (V), the enthalpy and the Gibbs function are functions of a force variable (p).

Thermal variables: whereas the internal energy and the enthalpy are functions of the entropy, the Helmholtz and Gibbs free energy functions are functions of the temperature.

If one is analyzing a process with, for example, *constant* temperature, it makes sense to use either the Helmholtz or Gibbs free energy functions, so that there is only one variable to consider.

Note that the temperature is an observable property and can be controlled to some extent. Values for the entropy, on the other hand, cannot be assigned arbitrary values in experiments. For this reason a description in terms of the free energy, for example, is often more useful than a description in terms of the internal energy.

4.3.2 Irreversible Processes

Consider now an irreversible process.

The Internal Energy

One has $\delta W = dU - \theta dS + \theta \delta S^{(i)}$ and, with the internal energy again a function of the entropy and volume,

$$\delta W = \left[\left(\frac{\partial U}{\partial S} \right)_V - \theta \right] dS + \left(\frac{\partial U}{\partial V} \right)_S dV + \theta \delta S^{(i)} \quad (4.3.13)$$

Consider the case of pure heating $\delta W = dV = \delta S^{(i)} = 0$, so

$$\theta = \left(\frac{\partial U}{\partial S} \right)_V \quad (4.3.14)$$

as in the reversible case. This relation between properties is of course valid for any process, not necessarily a pure heating one. Thus

$$\delta W = \left(\frac{\partial U}{\partial V} \right)_S dV + \theta \delta S^{(i)} \quad (4.3.15)$$

Express the work in the form

$$\boxed{\begin{aligned} \delta W &= dW^{(q)} + \delta W^{(d)} \\ &= A^{(q)} dV + A^{(d)} dV \end{aligned}} \quad (4.3.16)$$

such that the **quasi-conservative force** $A^{(q)}$ is that associated with the work $W^{(q)}$ which is recoverable, whilst the **dissipative force** $A^{(d)}$ produces the work $W^{(d)}$ which is dissipated, i.e. associated with irreversibilities.

From 4.3.15,

$$A^{(q)} = \left(\frac{\partial U}{\partial V} \right)_S \quad (4.3.17)$$

and the **dissipative work** $\delta W^{(d)}$ is

$$\delta W^{(d)} = A^{(d)} dV = \theta \delta S^{(i)} \geq 0 \quad (4.3.18)$$

The name *quasi-conservative force* for the $A^{(q)}$ (here, actually a force per area) is in recognition that the internal energy plays the role of a potential in 4.3.17, but it is also a function of the entropy. It can be seen from Eqn. 4.3.17 that the quasi-conservative force is a state function, and equals $-p$ in a fully reversible process.

In the **isentropic** case, $dS = 0$, and one has

$$\delta W = dU + \theta \delta S^{(i)} \quad (4.3.19)$$

This shows that, in the isentropic case, the internal energy is that part of the work which is recoverable.

The Free Energy

Directly from $\Psi = U - \theta S$, with θ and V the independent variables,

$$\frac{\partial \Psi}{\partial \theta} = \left(\frac{\partial U}{\partial \theta} - \theta \frac{\partial S}{\partial \theta} \right) - S, \quad \frac{\partial \Psi}{\partial V} = \frac{\partial U}{\partial V} - \theta \frac{\partial S}{\partial V} \quad (4.3.20)$$

From the pure heating analysis given earlier, Eqn. 4.2.9-10, the term $\partial U / \partial \theta - \theta \partial S / \partial \theta$ is zero, so

$$S = - \left(\frac{\partial \Psi}{\partial \theta} \right)_V \quad (4.3.21)$$

as in the reversible case and

$$d\Psi = \left(\frac{\partial \Psi}{\partial V} \right)_\theta dV - S d\theta \quad (4.3.22)$$

The work can now be written again as Eqn. 4.3.16, but now with the quasi-conservative force given by {▲ Problem 3}

$$A^{(q)} = \left(\frac{\partial \Psi}{\partial V} \right)_\theta \quad (4.3.23)$$

The dissipative work is again given by 4.3.18. Also, $A^{(q)} = -p$ for a reversible process.

In the isothermal case, $d\theta = 0$,

$$\delta W = d\Psi + \theta \delta S^{(i)} \quad (4.3.24)$$

This shows that, in the isothermal case, the free energy is that part of the work which is recoverable.

The quasi-conservative forces for the internal energy and free energy are listed in Table 4.3.2. Note that expressions for quasi-conservative forces are not available in the case of the Enthalpy and Gibbs free energy since they do not permit in their expression increments in volume dV , which are required for expressions of work increment.

Thermo-dynamic potential	Differential relationship	Relations
$U(S, V)$	$dU = -pdV + \theta dS - \theta \delta S^{(i)}$	$\theta = \left(\frac{\partial U}{\partial S} \right)_V, A^{(q)} = \left(\frac{\partial U}{\partial V} \right)_S$
$\Psi(\theta, V) = U - \theta S$	$d\Psi = -pdV - Sd\theta - \theta \delta S^{(i)}$	$S = -\left(\frac{\partial \Psi}{\partial \theta} \right)_V, A^{(q)} = \left(\frac{\partial \Psi}{\partial V} \right)_\theta$

Table 4.3.2: Quasi-Conservative Forces for Irreversible Processes,

$$\delta W = A^{(q)} dV + \theta \delta S^{(i)} = -pdV$$

4.3.3 The Legendre Transformation

The thermodynamic functions can be transformed into one another using a mathematical technique called the **Legendre Transformation**. The Legendre Transformation is discussed in detail in Part IV, where it plays an important role in Plasticity Theory, and other topics. For the present purposes, note that the Legendre transformation of a function $f(x, y)$ is the function $g(\alpha, \beta)$ where

$$g(\alpha, \beta) = \alpha x + \beta y - f(x, y) \quad (4.3.25)$$

and

$$\alpha = \frac{\partial f}{\partial x}, \beta = \frac{\partial f}{\partial y}, \quad x = \frac{\partial g}{\partial \alpha}, y = \frac{\partial g}{\partial \beta} \quad (4.3.26)$$

When only one of the two variables is switched, the transform reads

$$g(\alpha, y) = \alpha x - f(x, y) \quad (4.3.27)$$

where

$$\alpha = \frac{\partial f}{\partial x}, \quad x = \frac{\partial g}{\partial \alpha} \quad (4.3.28)$$

For example, if one has the function $U(S, V)$ and wants to switch the independent variable from S to θ , Eqn. 4.3.27 leads one to consider the new function

$$g(\theta, V) = \theta S - U(S, V) \quad (4.3.29)$$

and Eqns. 4.3.28 give

$$\theta = \left(\frac{\partial U}{\partial S} \right)_V \quad \text{and} \quad S = \left(\frac{\partial g}{\partial \theta} \right)_V \quad (4.3.30)$$

It can be seen that $g(\theta, V)$ is the negative of the Helmholtz free energy and the two differential relations in 4.3.30 are contained in Table 4.3.1.

4.3.4 Problems

1. By considering reversible processes, derive the differential relationships and the Maxwell relations given in Table 4.3.1 for (a) the enthalpy, (b) the Gibbs free energy
2. Let the two independent variables be V and θ . Consider the internal energy, $U = U(V, \theta)$. Use the pure heating example considered in §4.2 to show that the quasi-conservative force of Eqn. 4.3.17 can also be expressed as

$$A^{(q)} = \left(\frac{\partial U}{\partial V} - \theta \frac{\partial S}{\partial V} \right)_\theta$$

3. Show that Eqn. 4.3.22 leads to Eqn. 4.3.23.
4. Use the Legendre Transformation rule to transform the Helmholtz free energy $\Psi(\theta, V)$ into a function of the variables θ and σ . Derive also the two differential relations analogous to Eqns. 4.3.30. Show that this new function is the negative of the Gibbs energy (use the relation $\Psi = U - \theta S$), where $\sigma = -p$, and that the two differential relations correspond to two of the relations in Table 4.3.1.
5. Use the Legendre Transformation rule to transform the enthalpy $H(S, p)$ into a function of the variables S and V . Show that this new function is the negative of the internal energy, and that the two differential relations correspond to two of the relations in Table 4.3.1.