

THERMODYNAMIC POTENTIALS

- ✘ Thermodynamic potentials are state functions that, together with the corresponding equations of state, describe the equilibrium behavior of a system as a function of so-called "natural variables". The natural variables are a set of appropriate variables that allow to compute other state functions by partial differentiation of the thermodynamic potentials.

INTERNAL ENERGY U

The basic relation of thermodynamics is given by the equation

$$dU = TdS + \sum_{i=1}^m F_i dq_i + \sum_{j=1}^{\alpha} \mu_j dN_j, \quad (5.1)$$

where $\{F, q\}$ denote the set of conjugate intensive and extensive variables that characterize a system. For instance, for a gas

$$\{F, q\} \rightarrow \{-P, V\},$$

for a magnetic system

$$\{F, q\} \rightarrow \{\mathcal{B}, \mathcal{M}\}.$$

In (5.1), N is the number of particles in the system (an extensive variable); the index j ($j = 1, \dots, \alpha$) denotes different sets of particles that may constitute the system.

Chemical potential μ (an intensive variable): is defined as the energy needed to add a particle to a thermally and mechanically isolated system.

The last term in eq. (5.1), μdN , is needed if the number of particles in the system is not kept constant, i.e. if particles enter or leave the system.

For a gas, eq. (5.1) is written as

$$dU = TdS - PdV + \sum_{j=1}^{\alpha} \mu_j dN_j,$$

which means that

$$U = U(S, V, N)$$

Since dU is a total differential, through differentiation of U as a function of S , V , and N one obtains thermal and caloric equations of state:

$$\begin{aligned} T &= \left(\frac{\partial U}{\partial S} \right)_{V,N}, \\ -P &= \left(\frac{\partial U}{\partial V} \right)_{S,N}, \\ \mu_j &= \left(\frac{\partial U}{\partial N_j} \right)_{S,N,N_{i \neq j}}. \end{aligned}$$

The experimentally important *response* functions are obtained by second-order differentiation:

$$\begin{aligned} \left(\frac{\partial^2 U}{\partial S^2} \right)_{V,N} &= \left(\frac{\partial T}{\partial S} \right)_{V,N} = \left[\left(\frac{\partial S}{\partial T} \right)_{V,N} \right]^{-1} = \frac{T}{C_V} \Rightarrow \\ &\Rightarrow \boxed{C_V = T \left[\left(\frac{\partial^2 U}{\partial S^2} \right)_{V,N} \right]^{-1}}, \end{aligned}$$

$$\begin{aligned} \left(\frac{\partial^2 U}{\partial V^2}\right)_{S,N} &= -\left(\frac{\partial P}{\partial V}\right)_{S,N} = \frac{1}{Vk_S} \Rightarrow \\ &\Rightarrow \boxed{k_S = \frac{1}{V} \left[\left(\frac{\partial^2 U}{\partial V^2}\right)_{S,N}\right]^{-1}} \end{aligned} \quad (5.2)$$

Maxwell relations

A *Maxwell relation* follows from the differentiability of U :

$$\begin{aligned} \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right) &= \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right) \Rightarrow \\ &\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad (\text{Maxwell relation}). \end{aligned} \quad (5.3)$$

Example: monoatomic ideal gas. The behavior of a monoatomic ideal gas obeys the following relations:

$$PV = nRT,$$

$$U = \frac{3}{2}nRT,$$

$$C_V = \frac{3}{2}nR.$$

Let us use this information and derive an expression for U in terms of its natural variables:

$$dS = \frac{dU + PdV}{T} = C_V \frac{dT}{T} + nR \frac{dV}{V},$$

$$\begin{aligned} S(T, V) &= C_V \ln \left(\frac{T}{T_0} \right) + nR \ln \left(\frac{V}{V_0} \right) + S_0 \\ &= C_V \ln \left(\frac{U}{U_0} \right) + nR \ln \left(\frac{V}{V_0} \right) + S_0, \end{aligned}$$

$$\frac{S - S_0}{C_V} = \ln \left(\frac{U}{U_0} \right) + \frac{nR}{C_V} \ln \left(\frac{V}{V_0} \right). \quad (5.4)$$

Since

$$\begin{aligned} nR &= C_P - C_V \Rightarrow \\ \Rightarrow \frac{nR}{C_V} &= \frac{C_P - C_V}{C_V} = \gamma - 1 = \frac{5}{3} - 1 = \frac{2}{3}, \end{aligned}$$

we can write eq. (5.4) as

$$e^{\frac{S - S_0}{C_V}} = \left(\frac{U}{U_0} \right) \left(\frac{V}{V_0} \right)^{\frac{nR}{C_V}},$$

from which

$$\boxed{U(S, V) = U_0 \left(\frac{V_0}{V} \right)^{\gamma - 1} e^{\frac{S - S_0}{C_V}}} \quad (5.5)$$

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follows. Eq. (5.5) is the fundamental equation for the ideal gas, with $U(S, V)$ as the thermodynamic potential and S, V as independent natural variables.

Corollary: the natural variables for U are S and V , which means that if the function $U(S, V)$ is known for a given system we can obtain all the thermodynamic properties of the system through the differentiation of $U(S, V)$.

On the contrary, in the equation of state

$$U = U(T, V, N) \quad (5.6)$$

U is *not* an appropriate thermodynamic potential any more since from the first derivatives of eq. (5.6),

$$\left(\frac{\partial U}{\partial T} \right)_V = C_V$$

and

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

If we rewrite eq. (5.1) as

$$dS = \frac{1}{T}dU + \frac{1}{T}PdV - \frac{1}{T} \sum_{j=1}^{\alpha} \mu_j dN_j,$$

it becomes clear that

$$S = S(U, V, N)$$

is also a thermodynamic potential.

Note the analogy between classical mechanics and thermodynamics:

	Classical mechanics	Thermodynamics
Potential	$V(x, y, z)$	$U(S, V, N)$
Independent variables	x, y, z	S, V, N
Dependent variables obtained differentiating	$F_x = -\frac{\partial V}{\partial x}, \dots$	Maxwell relations: $P = -\left(\frac{\partial U}{\partial V}\right)_S, \dots$

LEGENDRE TRANSFORMATION

A disadvantage of using $U(S, V, N)$ as a thermodynamic potential is that the natural variable S is difficult to control in the lab. For practical purposes, it is more convenient to deal with other thermodynamic potentials that can be defined by making use of the *Legendre transformation*.

A thermodynamic potential for a system with variable number of particles should depend on $\{\mu, N\}$ as well as a thermal variable and a mechanical variable, which can be (for a gas):

thermal:	S (extensive)	T (intensive)
mechanical:	V (extensive)	P (intensive)

HELMHOLTZ FREE ENERGY

There are four possible combinations of these variables:

Intensive variables

$$\boxed{P} \rightarrow$$
$$\downarrow$$

ENTHALPY $H(S, P)$

Extensive variables

$$\leftarrow \boxed{S}$$
$$\downarrow$$

GIBBS ENTHALPY
 $G(T, P)$

INTERNAL ENERGY
 $U(S, V)$

$$\uparrow$$
$$\boxed{T} \rightarrow$$

FREE ENERGY $F(T, V)$

$$\leftarrow \boxed{V}$$
$$\uparrow$$

Legendre transformation (Reminder):

Consider a function $f = f(x)$ with the differential

$$df = \frac{df}{dx} dx = u dx.$$

We want to find a function $g = g(u)$ such that

$$\frac{dg}{du} = \pm x.$$

Function $g(u)$ can be found in the following way:

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Function $g(u)$ can be found in the following way:

$$df = u dx = d(ux) - x du$$

$$\Rightarrow d(f - ux) = -x du$$

$$\Rightarrow \frac{d}{du}(f - ux) = -x.$$

We define

$$g(u) = f(x) - ux = f(x) - x \frac{df}{dx}$$

as the Legendre transformation of $f(x)$.

HELMHOLTZ FREE ENERGY

By replacing the independent variable S by T in $U(S, V, N)$, we define the *free energy* F :

$$F = U - S \left(\frac{\partial U}{\partial S} \right)_{V, N} = U - TS$$

$$F = F(T, V, N) \rightarrow \text{Free energy.}$$



In

$$dF = dU - d(TS) = dU - SdT - TdS$$

we substitute dU from eq. (5.1) and get

$$dF = -SdT - PdV + \sum_{j=1}^{\alpha} \mu_j dN_j.$$

The natural variables of the free energy are $\{T, V, N\}$. The *dependent* variables are obtained out of the first derivatives:

$$-S = \left(\frac{\partial F}{\partial T} \right)_{V, N}, \quad P = - \left(\frac{\partial F}{\partial V} \right)_T \rightarrow \text{thermal state equations}$$

and

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \rightarrow \text{Maxwell relation.}$$

ENTHALPY

is obtained when we substitute the variable V by P in $U(S, V, N)$:

$$\boxed{H = U + PV}$$

The total differential of H is derived as follows.

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

$$\begin{aligned} dH = dU + d(PV) &= dU + VdP + PdV \\ &= TdS - PdV + \sum_{j=1}^{\alpha} \mu_j dN_j + VdP + PdV \quad \Rightarrow \end{aligned}$$

$$\Rightarrow \boxed{dH = TdS + VdP + \sum_{j=1}^{\alpha} \mu_j dN_j}$$

The natural variables of the enthalpy are $\{S, P, N\}$. Out of the first order derivatives we obtain

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N}$$

$$V = \left(\frac{\partial H}{\partial P}\right)_{S,N}$$

and the Maxwell relation

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{P,N}}$$

GIBBS ENTHALPY

We obtain the Gibbs enthalpy

$$G = G(T, P, N)$$

by replacing S by T and V by P in $U(S, V, N)$:

$$G = U - S \left(\frac{\partial U}{\partial S} \right)_{V,N} - V \left(\frac{\partial U}{\partial V} \right)_{S,N} \Rightarrow$$
$$\Rightarrow \boxed{G = U - TS + PV}$$

The total differential of the Gibbs enthalpy:

$$dG = dU - TdS - SdT + PdV + VdP,$$

$$dG = TdS - PdV + \sum_{j=1}^{\alpha} \mu_j dN_j - TdS - SdT + PdV + VdP,$$

$$\boxed{dG = -SdT + VdP + \sum_{j=1}^{\alpha} \mu_j dN_j}$$

Out of the first derivatives of G , we obtain

$$S = - \left(\frac{\partial G}{\partial T} \right)_{P,N},$$

$$V = \left(\frac{\partial G}{\partial P} \right)_{T,N},$$

and the Maxwell relation

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

THANK YOU