Lecture

Thermodynamics

We want to connect statistical physics with Thermodynamics. Going back to the Table of useful thermodynamics quantities, we notice that statistical Physics produces the partition functions

$\Omega(E,V,N)$ from the microcanonical distribution

$Z(T,V,N)$ from the canonical distribution

$\Lambda(T,V,\mu)$ from the grand canonical distrib.

Notice that the thermodynamic variables differ for different statistical distributions

(E,V,N) microcanonical

(T,V,N) canonical

(T,V,μ) grand canonical

Each statistical distribution corresponds to an experimental constrain isolated system — microcononi cal

heat bath contact — Cononi cal

heat bath and particle reservoire contact — grand canonical

The logarithm of each partition function was important (see Table of useful thermodynamic quantities) in deriving: pressure, heat capacity, average internal energy and so on.
In Thermodynamics the logarithm of the partition functions is viewed as a function of the thermodynamic variables and are called thermodynamic potentials

$$S(E,V,N) = k \ln \Omega(E,V,N)$$ microcononi cal

$$F(T,V,N) = -kT \ln Z_1(T,V,N)$$ Cononi cal

$$L(T,V,\mu) = -kT \ln \Delta(T,V,\mu$$ grand canonical

It is clear that from a thermodynamic point of view the information about the system is contained in the thermodynamic potentials.

There are two important questions regarding the thermodynamic potentials

1) Suppose we cannot derive mathematically the partition function from statistical physics (the problem is too complicated). Can we overcome this difficulty through experimental measurements? If yes, what should we measure.

2) Suppose we compute succesfully the canonical thermodynamic potential using the distribution, and thus find F(T, V, N). To get the potential L(T, V, μ) do we need to start the computations again from scratch for the grand canonical distribution, or we can use the available result F(T, V, N)?

We will respond to question 2) first.

ANSWER TO QUESTION 2

In principle we cannot obtain $L(T,V,\mu)$ from $F(T,V,N)$. However, in the thermodynamic limit (when the number of particle N is very big, the volome V is big, with a density $\rho = \frac{N}{V}$ kept at reasonable values) we can find $L(T,V,\mu)$ from $F(T,N,V)$. The logic is as follows

$$Z(T,V,N) = \sum_{\text{states } j} e^{-\beta E_j} \tag{1}$$

$$\Lambda(T,V,\mu) = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{\text{states } j_N} e^{-\beta E_{j_N}} \tag{2}$$

If one term from the first sum dominates the other terms in (2) we have

$$\underbrace{e^{\beta\mu N^*} \sum_{\text{states } j_{N^*}} e^{-\beta E_{j_{N^*}}}}_{\text{This } N^* \text{ is one number out of } 0,1,2,\cdots,\infty} \gg \underbrace{e^{\beta\mu N} \sum_{\text{states } j_N} e^{-\beta E_{j_N}}}_{\text{for all } N \text{ different that } N^*}$$

In this situation

$$\Lambda(T,V,\mu) \underset{\uparrow}{\simeq} e^{\beta\mu N^*} \sum_{\text{states } j'_{N^*}}' e^{-\beta E_{j_{N^*}}} \qquad (3)$$

approximation by neglecting all terms for $N=0,1,2,\ldots$, EXCEPT the term for $N=N^*$.

This approximation is very good for systems containing a large number of particles.

Thus

$$\ln\Lambda(T,V,\mu) \simeq \beta\mu N^* + \ln \underbrace{\sum_{\text{states } j'_{N^*}} e^{-\beta E_{j_{N^*}}}}_{Z(T,V,N^*)}$$

$$\ln\Lambda(T,V,\mu) \simeq \beta\mu N^* + \ln Z(T,V,N^*)$$

or, by multiplying on both sides by $-kT$, we get

$$L(T,V,\mu) \underset{\uparrow}{=} -\mu N^* + F(T,V,N^*) \qquad (4)$$

here I write equal because in Thermodynamics the system is considered at the limit $N\to\infty$.

To finish the problem we need N^* as a function of T, V, μ to insert in (4). But N^* was special in the sence that it maximized the term

$$e^{\beta\mu N}\sum_{\text{states } j_N}' e^{-\beta E_{j_N}}$$

So the derivative of this term with respect to N must be zero

$$\frac{d}{dN}\left(e^{\beta\mu N}\sum_{\text{states } j_N}' e^{-\beta E_{j_N}}\right) = 0 \qquad (5)$$

Condition (5) is an equation for N^*. It can be recasted as

$$-\beta\mu\, e^{-\beta\mu N} Z_N + e^{-\beta\mu N}\frac{\partial Z_N}{\partial N} = 0$$

$$\beta\mu Z_N = -\frac{\partial Z_N}{\partial N}$$

$$\mu = -kT\frac{\partial \ln Z_N}{\partial N} \qquad \left(\text{because } \beta = \frac{1}{kT}\right)$$

$$\mu = \frac{\partial F(T,V,N)}{\partial N} \qquad \text{Equation for } N^*.$$

Conclusion

To find $L(T,V,\mu)$ from $F(T,V,N)$, first solve for N from

$$\boxed{\mu = \left(\frac{\partial F(T,V,N)}{\partial N}\right)_{T,V} \qquad (5)}$$

and obtain $N(T,V,\mu)$ (this is N^*)

Insert then this $N(T,V,\mu)$ into (4)

$$\boxed{L(T,V,\mu) = -\mu N + F(T,V,N) \qquad (6)}$$

Notice that I do not use N^* as a notation in (5) and (6) because now is not necessary anymore to give a special name to the solution of equation (5).

The transformation from $F(T,V,N)$ to $L(T,V,\mu)$ following the procedure (5) and (6) is called a LEGENDRE TRANSFORMATION.

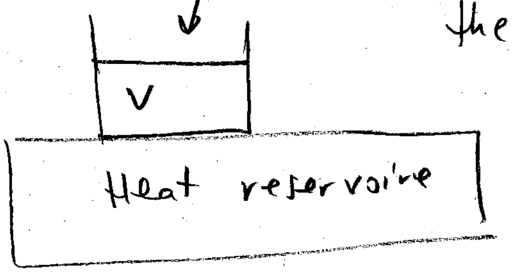
The idea is that the statistical physics approximation of one partition function with another produces at thermodynamic level a Legendre transformation.

Speaking in more general terms, the Legendre transformation relates thermodynamic variables and potentials through the use of partial derivatives, like in (5). There is a need thus in Thermodynamics to compute many partial derivatives. Because there are so many possible partial derivatives, the presentation of Thermodynamics becomes rapidly a jungle of symbols containing ∂, ∂^2 and so on. A systematic classification of all thermodynamic partial derivatives is thus important. Before we go into the classification of these partial derivatives we will talk more about the Legendre transformation, by first summarizing the Legendre transformation from microcanonical to the Legendre transformation from microcanonical to Canonical distribution.

	Given	Find	Legendre transformation
STATISTICAL PHYSICS PERSPECTIVE	$\Omega(E,V,N)$	$Z(T,V,N)$	$\beta = \dfrac{\partial \ln \Omega(E)}{\partial E}$ Equation for $E(T,V,N)$ Substitute this solution into $\ln Z(T,V,N) = -\beta E + \log \Omega(E)$ this was called E_{max} in the Microcanonical distribution lecture

	Given	Find	Legendre transformation
THERMODYNAMIC PERSPECTIVE	$S(E,V,N)$ remember that $S = k \ln \Omega$	$F(T,V,N)$ remember that $F = -kT\ln Z$	$\frac{1}{T} = \frac{\partial S(E,V,N)}{\partial E}$ Equation for $E(T,V,N)$ Substitute this solution into $F(T,V,N) = E - T S(E,V,N)$
STATISTICAL PHYSICS PERSPECTIVE	$Z(T,V,N)$	$\Omega(E,V,N)$	$E = -\frac{\partial \ln Z(\beta,V,N)}{\partial \beta}$ Equation for $\beta(E,V,N)$ Substitute this solution into $\ln \Omega = \beta E + \ln Z(\beta,V,N)$
THERMODYNAMICS PERSPECTIVE	$F(T,V,N)$	$S(E,V,N)$	$E = T \frac{\partial F(T,V,N)}{\partial T}$ Equation for $T(E,V,N)$ Substitute this solution into $S = \frac{1}{T}E - \frac{1}{T}F(T,V,N)$

A similar table can be constructed for canonical to grand canonical and for microcanonical to grand canonical. Moreover, there are other distribution in equilibrium statistical physics that generates other thermodynamic potentials. For example, a system can be in contact with a heat bath that keeps an average energy constant and with a "volume reservoire" that keeps a constant average volume



the volume can vary, but the atmospheric pressure p keeps the inside pressure constant.

The partition function for this situation is

$$Y(T,p,N) = \int_0^\infty e^{-\beta p V} Z(T,V,N)\, dV$$

the number of particle is fixed

The Thermodynamic potential is known as Gibbs potential

$$\boxed{G(T,p,N) = -kT \ln Y(T,P,N)}$$

This Gibbs potential is related with the Helmholtz potential $F(T,V,N)$ by:

$$p = -\frac{\partial F}{\partial V}$$ (Equation for V)

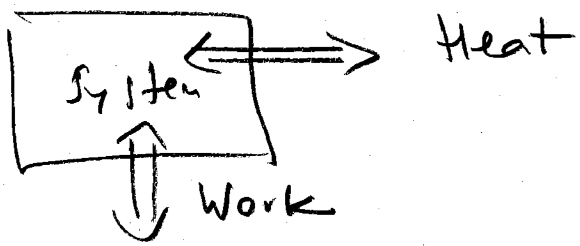
(Insert the above solution into)

$$G = pV + F$$

Conclusion to the answer to question 2: there are many potential in thermodynamics which are related through Legendre transformation. If we know one potential, we can find the other potentials.

Answer to Question 1

We can measure the heat exchanged and the work exchanged by the system with the exterior



We showed, in the Lecture "Pressure", that the <u>change</u> in the internal energy (which is the average energy from the statistical physics point of view) when the <u>thermodynamical variables</u> change (driving the system all the time through a sequence of equilibrium thermodynamical states) is given in the grand canonical distribution by:

$$dU = \underbrace{T\,dS}_{\text{Heat exchanged}} + \underbrace{\mu\, d\langle N\rangle - p\,dV - \langle M\rangle_{GC}\, dB}_{\text{Work exchanged}}$$

The internal energy is a function of $\overline{T, V, \mu, B}$ ← for grand canonical and other variables which we will not mention here for the sake of simplicity. Adding other variables will not change the logical construction. Because U is a function of T, V, μ, B, we have

$$dU = \frac{\partial U}{\partial T}\,dT + \frac{\partial U}{\partial V}\,dV + \frac{\partial U}{\partial \mu}\,d\mu + \frac{\partial U}{\partial B}\,dB$$

the interpretation of du is, obviously,

$$dU = U_{final} - U_{initial}$$

"final" and "initial" are two very closely related thermodynamic states.

To go from "initial" to "final", we
make a change in the temperature, dT, in
the chemical potential dμ
the volume dV, in the
magnetic field dB. [Remark:
and in the
considered
in this course, for simplicity we
only those situation for which B ≅ H. The
treatment of the thermodinamics of sytems
in magnetic fields is more complex than
the simplistic approach we discussed so far.]

Now, the heat exchanged Tds is NOT a
difference between a final and an initial
thermodynamic state of some function

$$Tds \neq \overset{\uparrow}{df}$$

there is no function $f(T, V, \mu, B)$
so that $Tds = df$

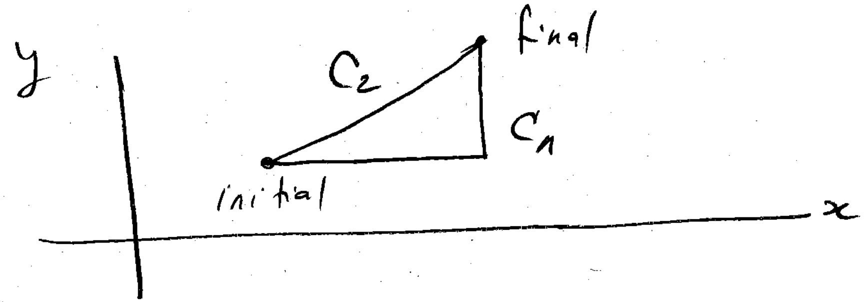
To distinguish between these situations, du is called an EXACT DIFFERENTIAL and Tds an INEXACT DIFFERENTIAL.

A mathematical example

Consider the differential in two coordinates (x,y)

$$yx\,dx + x^2 dy$$

The integral of this differential depends on the curve of integration that connects the "initial" with the "final" point



$$\int_{C_1} yx\,dx + x^2 dy \neq \int_{C_2} yx\,dx + x^2 dy$$

the differential is INEXACT. For a differential of the form

$$f(x,y)\,dx + g(x,y)\,dy$$

a necessary and sufficient condition to be exact is

$$\frac{\partial f}{\partial y} = \frac{\partial g}{\partial x}$$

For our example

$$\frac{\partial (yx)}{\partial y} \neq \frac{\partial (x^2)}{\partial x}$$

— end of the math example —

We will denote the inexact differentials with $đ$

$$đQ = T\,dS$$ infinitesimal heat exchange

$$đW = \mu\, d\langle N\rangle - p\,dV - \langle M\rangle_{GC}\, dB$$

So

$$\boxed{dU = đQ + đW}$$ the First Law of Thermodynamics

<u>Remark</u> The Second Law of Thermodynamics is principle of maximum entropy which we used to derive the statistical distributions.

In practice we measure $\text{đ}Q$ and $\text{đ}W$ volume V, pressure p, temperature T, the magnetic field B. Frome these measurement we can tabulate a series of susceptibilities

Susceptibility		
Specific Heat at constant volume or constant pressure	$C_p = T\left(\frac{\partial S}{\partial T}\right)_p$ $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$	$\longrightarrow$ remember that $\text{đ}Q = TdS$ so $C_p = \frac{\text{đ}Q}{dT}\Big\vert_p$
Thermal expansion coefficient at constant pressure or constant entropy [entropy does not change when $\text{đ}Q = 0$]	$\beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ $\beta_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S$	this is **not** the β from statistical physics. Here it is a thermodynamic notation
Compressibility at constant temperature or constant entropy	$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ $\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$	

Susceptibility	
Heat of pressure variation at constant temperature or constant volume	$\Gamma_T = T\left(\frac{\partial S}{\partial p}\right)_T$ $\Gamma_V = T\left(\frac{\partial S}{\partial p}\right)_V$

If we include the magnetic field B then we can define magnetic susceptibilities; if we include the electric field E then we define electric susceptibilities and so on.

The GOAL is now: find all the other partial derivatives of thermodynamic potentials in terms of the measured susceptibilities, the entropy S (measured by the heat exchange $dQ = TdS$) temperature T, volume V, pressure p,

For example

$$\left(\frac{\partial G}{\partial p}\right)_V = V - \frac{S K_T}{\beta_p}$$

this is not Boltzmann constant. It is a compressibility

This goal is achieved through a series a partial derivative rules, which are presented in what follows.

6.10 THE USE OF THERMODYNAMIC TABLES

In making any practical use of thermodynamics one must refer to standard compilations of physical properties, such as the *Handbook of Chemistry and Physics*, to obtain the essential thermodynamic functions for any particular substance. In most cases, the physical properties are tabulated as functions of temperature and pressure, for the simple reason that, experimentally, those are usually the variables that are easiest to accurately control. Not every conceivable physical property is tabulated. For a given substance, one can typically find the molar entropy and the molar volume as functions of p and T. Also commonly available are the constant pressure molar heat capacity,

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p \tag{6.62}$$

the temperature coefficient of expansion,

$$\beta_p = V^{-1}\left(\frac{\partial V}{\partial T}\right)_p \tag{6.63}$$

and the isothermal compressibility,

$$\kappa_T = -V^{-1}\left(\frac{\partial V}{\partial p}\right)_T \tag{6.64}$$

The five quantities S, V, C_p, β_p, and κ_T are equivalent to the set of first and second derivatives of the molar Gibbs free energy. In particular, $S = -(\partial G/\partial T)$, $V = (\partial G/\partial p)$, $C_p = -T(\partial^2 G/\partial T^2)$, $\beta_p = (\partial^2 G/\partial T\,\partial p)/V$, and $\kappa_T = -(\partial^2 G/\partial p^2)/V$, as can be verified from Eq. (6.57). Therefore, in terms of these five quantities, it should be possible to express any quantity that involves first and second derivatives of any thermodynamic potentials as a function of p and T. This is enough to evaluate almost any quantity that is likely to appear in a normal thermodynamic analysis.

The ENTALPY $H(S,P)$
defined
by
$H(S,P)=U+PV$
The E
here is
our U
(internal
energy)

6.11 TRANSFORMATION OF VARIABLES

The thermodynamic space of a simple substance is three dimensional. However, when we fix the particle number at one mole, as we have, the set of possible equilibrium states becomes two dimensional. That means that fixing the values of any two independent thermodynamic parameters is enough to define the state of the substance and hence to determine the values of all other thermodynamic variables. It is not uncommon, in practical calculations, for very strange combinations of variables to appear naturally. For example, in certain processes one can show that the enthalpy H remains constant (see Problem 6.12). Determining how the temperature varies with the pressure in such a process requires that one calculate the partial derivative $(\partial T/\partial p)_H$, which is just the partial derivative of the function $T(p,H)$. It is therefore important that one be able to convert almost any conceivable combination of partial derivatives of thermodynamic variables to some standard form in which they may be evaluated. In this section a systematic procedure will be given to convert any expression involving partial derivatives of the thermodynamic quantities p, T, S, V, E, F, H, G, and μ into an expression involving only p and T and the five "handbook variables," S, V, C_p, β_p, and κ_T. This is equivalent to evaluating an arbitrary partial derivative in the p-T representation. The procedure makes use of the three types of information listed here.

1. Differential relations

$$\begin{aligned} dE &= T\,dS - p\,dV \\ dF &= -S\,dT - p\,dV \\ dH &= T\,dS + V\,dp \\ dG &= -S\,dT + V\,dp \end{aligned} \tag{6.65}$$

Of these, only the first needs to be memorized; the others are obtained by Legendre transformations, which give predictable sign changes in the terms.

2. Definitions of C_p, β_p, and κ_T

$$\begin{aligned} C_p &= T\left(\frac{\partial S}{\partial T}\right)_p \\ \beta_p &= V^{-1}\left(\frac{\partial V}{\partial T}\right)_p = -V^{-1}\left(\frac{\partial S}{\partial p}\right)_T \\ \kappa_T &= -V^{-1}\left(\frac{\partial V}{\partial p}\right)_T \end{aligned} \tag{6.66}$$

In the formula for β_p one of the Maxwell relations has been used.

3. Partial derivative identities Given any set of variables x, y, z, and w that have the property that the values of any two of the variables determine those of the others, then

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \tag{6.67}$$

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y} \tag{6.68}$$

and

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{\left(\frac{\partial x}{\partial w}\right)_z}{\left(\frac{\partial y}{\partial w}\right)_z} \tag{6.69}$$

The first identity follows from the fact that, once the value of z has been fixed, x becomes a function of y and vice versa. But, for functions of one variable, $dx/dy = (dy/dx)^{-1}$.

The second identity can be derived from the differential relation

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{6.70}$$

If we set dz equal to zero, then the ratio of dx to dy is just $(\partial x/\partial y)_z$. This gives

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x = 0 \tag{6.71}$$

which is equivalent to the desired identity.

The third identity can be derived by considering two neighboring points that have the same values of z. The changes in x, y, and w are related by

$$dx = \left(\frac{\partial x}{\partial w}\right)_z dw, \quad dy = \left(\frac{\partial y}{\partial w}\right)_z dw, \quad \text{and} \quad \left(\frac{\partial x}{\partial y}\right)_z = \frac{dx}{dy} \tag{6.72}$$

from which the identity follows immediately.

Our task is now to convert any partial derivative expression, such as $(\partial\mu/\partial p)_H$ or $(\partial S/\partial V)_p$, into an expression involving p, T, S, V, and derivatives of the form

$$\left(\frac{\partial(S \text{ or } V)}{\partial(p \text{ or } T)}\right)_{(T \text{ or } p)} \tag{6.73}$$

which can all be written in terms of handbook quantities. We will do this in two stages. Calling p, T, S, and V the *good* variables and E, F, H, G, and μ the *bad* variables, we will first eliminate all bad variables in favor of good variables. Then we will transform any resulting partial derivatives, which will only involve good variables, to the specific form shown in Eq. (6.73).

In eliminating the bad variables, the chemical potential μ is a special case. It is eliminated by using the fact that (see Problem 6.10) the chemical potential of any substance is always equal to the molar Gibbs free energy. Thus μ is simply replaced by $\hat{G}$. We now introduce the convention that a and b denote good variables, α denotes a bad variable, and x, y, and z may be either good or bad.

To transform a term of the form $(\partial\alpha/\partial x)_y$, one uses the corresponding differential relation. For example, the relation, $dH = T\,dS + V\,dp$ gives

$$\left(\frac{\partial H}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y + V\left(\frac{\partial p}{\partial x}\right)_y \tag{6.74}$$

Notice that this will never introduce any new bad variables.

To eliminate a term of the form $(\partial a/\partial\alpha)_x$, one uses the first partial derivative identity.

$$\left(\frac{\partial a}{\partial \alpha}\right)_x = \frac{1}{\left(\frac{\partial \alpha}{\partial a}\right)_x} \tag{6.75}$$

followed by the appropriate differential relation to eliminate α. These two procedures will eliminate bad variables as either numerators or denominators in partial derivative expressions. The only remaining possibilities are expressions of the form $(\partial a/\partial b)_\alpha$. These are converted by the second partial derivative identity.

$$\left(\frac{\partial a}{\partial b}\right)_\alpha = -\frac{\left(\frac{\partial \alpha}{\partial b}\right)_a}{\left(\frac{\partial \alpha}{\partial a}\right)_b} \tag{6.76}$$

followed by the use of a differential relation to eliminate α entirely.

With these procedures we can reduce any partial derivative to ones containing only p, T, S, and V. If these are not in the desired form, shown in Eq. (6.73), then they can be converted to that form as follows.

For an expression of the form

$$\left(\frac{\partial(p \text{ or } T)}{\partial(S \text{ or } V)}\right)_{(T \text{ or } p)} \tag{6.77}$$

we use the first partial derivative identity.

For an expression of the form

$$\left(\frac{\partial(p \text{ or } T}{\partial(T \text{ or } p)}\right)_{(S \text{ or } V)} \tag{6.78}$$

we use the second partial derivative identity. The remaining possibilities are expressions of the form

$$\left(\frac{\partial(S \text{ or } V)}{\partial(p \text{ or } T)}\right)_{(V \text{ or } S)} \quad \text{or} \quad \left(\frac{\partial(S \text{ or } V)}{\partial(V \text{ or } S)}\right)_{(p \text{ or } T)} \tag{6.79}$$

The first of these is converted to the standard form by the procedure illustrated.

$$\left(\frac{\partial S}{\partial p}\right)_V \equiv \frac{\partial S(p,V)}{\partial p} = \frac{\partial S(p,T(p,V))}{\partial p} = \left(\frac{\partial S}{\partial p}\right)_T + \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V \tag{6.80}$$

which reduces it to the immediately previous case. The second case requires the third partial derivative identity.

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial V}{\partial p}\right)_T} \tag{6.81}$$

6.12 A FORMULA FOR $C_p - C_v$

An important example of the foregoing type of analysis is the following derivation of a formula for the difference between the constant pressure and constant volume molar specific heats. The definition of C_v is

$$C_v = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \tag{6.82}$$

But

$$\begin{aligned} \left(\frac{\partial S}{\partial T}\right)_V &= \frac{\partial S(T,V)}{\partial T} = \frac{\partial S(T,p(V,T))}{\partial T} \\ &= \left(\frac{\partial S}{\partial T}\right)_p + \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V \end{aligned} \tag{6.83}$$

Using the facts that

$$T\left(\frac{\partial S}{\partial T}\right)_p = C_p, \tag{6.84}$$

Table S6.2 The Bridgeman transformation table*

$(\partial T)_p$	$-(\partial p)_T$	$\longrightarrow$	1
$(\partial V)_p$	$-(\partial p)_V$	$\longrightarrow$	$V\beta$
$(\partial S)_p$	$-(\partial p)_S$	$\longrightarrow$	C/T
$(\partial E)_p$	$-(\partial p)_E$	$\longrightarrow$	$C - pV\beta$
$(\partial H)_p$	$-(\partial p)_H$	$\longrightarrow$	C
$(\partial G)_p$	$-(\partial p)_G$	$\longrightarrow$	$-S$
$(\partial F)_p$	$-(\partial p)_F$	$\longrightarrow$	$-S - pV\beta$
$(\partial V)_T$	$-(\partial T)_V$	$\longrightarrow$	$V\kappa$
$(\partial S)_T$	$-(\partial T)_S$	$\longrightarrow$	$V\beta$
$(\partial E)_T$	$-(\partial T)_E$	$\longrightarrow$	$TV\beta - pV\kappa$
$(\partial H)_T$	$-(\partial T)_H$	$\longrightarrow$	$TV\beta - V$
$(\partial G)_T$	$-(\partial T)_G$	$\longrightarrow$	$-V$
$(\partial F)_T$	$-(\partial T)_F$	$\longrightarrow$	$-pV\kappa$
$(\partial S)_V$	$-(\partial V)_S$	$\longrightarrow$	$V^2\beta^2 - VC\kappa/T$
$(\partial E)_V$	$-(\partial V)_E$	$\longrightarrow$	$TV^2\beta^2 - VC\kappa$
$(\partial H)_V$	$-(\partial V)_H$	$\longrightarrow$	$TV^2\beta^2 - VC\kappa - V^2\beta$
$(\partial G)_V$	$-(\partial V)_G$	$\longrightarrow$	$SV\kappa - V^2\beta$
$(\partial F)_V$	$-(\partial V)_F$	$\longrightarrow$	$SV\kappa$
$(\partial E)_S$	$-(\partial S)_E$	$\longrightarrow$	$pV^2\beta^2 - pVC\kappa/T$
$(\partial H)_S$	$-(\partial S)_H$	$\longrightarrow$	$-VC/T$
$(\partial G)_S$	$-(\partial S)_G$	$\longrightarrow$	$SV\beta - VC/T$
$(\partial F)_S$	$-(\partial S)_F$	$\longrightarrow$	$pV^2\beta^2 + SV\beta - pVC\kappa/T$
$(\partial H)_E$	$-(\partial E)_H$	$\longrightarrow$	$pV^2\beta + pVC\kappa - VC - pTV^2\beta^2$
$(\partial G)_E$	$-(\partial E)_G$	$\longrightarrow$	$pV^2\beta + TSV\beta - VC - pSV\kappa$
$(\partial F)_E$	$-(\partial E)_F$	$\longrightarrow$	$pTV^2\beta^2 - pVC\kappa$
$(\partial G)_H$	$-(\partial H)_G$	$\longrightarrow$	$TSV\beta - VC - VS$
$(\partial F)_H$	$-(\partial H)_F$	$\longrightarrow$	$(TV\beta - V)(S + pV\beta) - pV\kappa$
$(\partial F)_G$	$-(\partial G)_F$	$\longrightarrow$	$pSV\kappa - SV - pV^2\beta$

*In this table $C \equiv C_p$, $\beta \equiv \beta_p$, and $\kappa \equiv \kappa_T$.

which shows that $S = C/3$.

Exercise 6.14 In Section 6.11 it was shown how an arbitrary partial derivative involving the variables p, T, S, V, E, F, H, G, and μ could be transformed into an expression involving p, T, and the five "handbook functions," S, V, C_p, β_p, and κ_T. In 1941, P. W. Bridgeman (*Physical Review*, 3, p. 273) published a table that allows the results of such a calculation to be written down immediately. The table is reproduced as Table S6.2, and its use is illustrated by two examples.

$$\left(\frac{\partial G}{\partial p}\right)_V \rightarrow \frac{(\partial G)_V}{(\partial p)_V} \rightarrow \frac{SV\kappa_T - V^2\beta_p}{-V\beta_p} = V - \frac{S\kappa_T}{\beta_p} \tag{S6.63}$$

and

$$\left(\frac{\partial F}{\partial V}\right)_p \rightarrow \frac{(\partial F)_p}{(\partial V)_p} \rightarrow \frac{-S-pV\beta_p}{V\beta_p} = -\frac{S}{V\beta_p} - p \tag{S6.64}$$

That is, we first replace the partial derivative $(\partial x/\partial y)_a$ by a fraction made up of the mathematically meaningless symbols $(\partial x)_a$ and $(\partial y)_a$. We look up each symbol in the table (it will always be found either in the first column or the second, never in both), and replace it by the quantity shown in the last column. The resulting fraction gives the value of the partial derivative in the p-T representation.

Work out each of the following partial derivatives, first using Bridgeman's table, and then using the method of Section 6.11. (a) $(\partial F/\partial S)_p$; (b) $(\partial E/\partial T)_G$.

Solution (a)

$$\left(\frac{\partial F}{\partial S}\right)_p \rightarrow \frac{(\partial F)_p}{(\partial S)_p} = -\frac{S+pV\beta_p}{C_p/T} \tag{S6.65}$$

To verify this by the method of Section 6.11, we first note that $dF = -S\,dT - p\,dV$, and thus

$$\left(\frac{\partial F}{\partial S}\right)_p = -S\left(\frac{\partial T}{\partial S}\right)_p - p\left(\frac{\partial V}{\partial S}\right)_p \tag{S6.66}$$

The first expression is eliminated using

$$\left(\frac{\partial T}{\partial S}\right) = \frac{1}{(\partial S/\partial T)_p} = \frac{T}{C_p} \tag{S6.67}$$

The second expression requires the third partial derivative identity.

$$\left(\frac{\partial V}{\partial S}\right)_p = \frac{(\partial V/\partial T)_p}{(\partial S/\partial T)_p} = \frac{V\beta_p}{C_p/T} \tag{S6.68}$$

The result agrees with Bridgeman's table. (b) By Bridgeman's table,

$$\begin{aligned}\left(\frac{\partial E}{\partial T}\right)_G \rightarrow \frac{(\partial E)_G}{(\partial T)_G} &= \frac{-pV^2\beta_p - TSV\beta_p + VC_p + pSV\kappa_T}{V} \\ &= C_p + pS\kappa_T - pV\beta_p - TS\beta_p\end{aligned} \tag{S6.69}$$

By Section 6.11, we first use $dE = T\,dS - p\,dV$.

$$\left(\frac{\partial E}{\partial T}\right)_G = dT\left(\frac{\partial S}{\partial T}\right)_G - p\left(\frac{\partial V}{\partial T}\right)_G \tag{S6.70}$$

Both terms on the right-hand side require the second partial derivative identity.

$$\left(\frac{\partial S}{\partial T}\right)_G = -\frac{(\partial G/\partial T)_S}{(\partial G/\partial S)_T} \tag{S6.71}$$

and

$$\left(\frac{\partial V}{\partial T}\right)_G = -\frac{(\partial G/\partial T)_V}{(\partial G/\partial V)_T} \tag{S6.72}$$

These are followed by use of the differential relation $dG = -S\,dT + V\,dp$, giving

$$\left(\frac{\partial G}{\partial T}\right)_S = -S + V\left(\frac{\partial p}{\partial T}\right)_S \tag{S6.73}$$

$$\left(\frac{\partial G}{\partial S}\right)_T = -S \cdot 0 + V\left(\frac{\partial p}{\partial S}\right)_T = 1/\beta_p \tag{S6.74}$$

$$\left(\frac{\partial G}{\partial T}\right)_V = -S + V\left(\frac{\partial p}{\partial T}\right)_V \tag{S6.75}$$

$$\left(\frac{\partial G}{\partial V}\right)_T = -S \cdot 0 + V\left(\frac{\partial p}{\partial V}\right)_T = -1/\kappa_T \tag{S6.76}$$

To transform the remaining expressions, we need the second partial derivative identity.

$$\left(\frac{\partial p}{\partial T}\right)_S = -\frac{(\partial S/\partial T)_p}{(\partial S/\partial p)_T} = \frac{C_p/T}{V\beta_p} \tag{S6.77}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \beta_p/\kappa_T \tag{S6.78}$$

Making all the back substitutions verifies Eq. (S6.68) (and gives one an appreciation for the efficiency of Bridgeman's table).