

A summary of Callan[†] on Thermoelectric Effects.

1. My first step was to go back to his chapter 2 to relearn the two basic representations for doing thermo:

(a) the energy representation, wherein $U = U(S, X_1, X_2, \dots)$ is the main object of interest, the X_i are the various extensive parameters like volume, and the first law of thermo has this form:

$$P_i = (dU/dX_i) = \text{generalized "force" intensive parameter}$$

$$P_0 = (dU/dS) = T, \text{ the temperature}$$

$$P_i = (dU/dN_i) = \mu_i, \text{ the chemical potential, example of intensive force}$$

$$dU = P_i dX_i = T dS + \text{rest} \quad \text{where} \quad T dS = dQ$$

(b) the entropy representation, wherein $S = S(U, X_1, X_2, \dots)$ is the main object of interest, the $X_0 = U$ now, and the others are the same as before. Then:

$$F_i = (dS/dX_i) = \text{general force in this representation} = -P_i/T \quad i \neq 0$$

$$F_0 = (dS/dU) = 1/T, \text{ the inverse temperature}$$

$$dS = F_i dX_i = (1/T) dU + \text{rest}$$

2. Next, we skip to chapter 16 where we learn about affinities and fluxes for two coupled systems (discrete, not yet continuous). Assume there is some extensive parameter X_k and related intensive force F_k . Then you can define:

$$f_k = F_k - F'_k = \text{the difference between the forces (affinity)}$$

$$J_k = (dX_k/dt) = \text{the flux related to the above.}$$

Think of a partitioned box that is not in TE. There is a net force on the sliding partition which causes it to move. Thus, the volumes on the two sides change, there is a dV/dt . This would be the flux resulting from the affinity.

Thus we are making a theory to describe things when we are close to but not in Thermal Equilibrium! Using the chain rule, you can show that:

$$dS/dt = f_k J_k$$

Ie, as things adjust (the partition moves) the total entropy must be increasing and this gives the rate at which it does so. Here S = entropy of both systems together. Note that entropy is not conserved in the way U is!

3. The next step is to extend these ideas to the continuum case where your system is a little differential piece of system in contact with the rest. Callan switches to lower-case extensive parameters defined as per volume. The above equations become:

$$\vec{f}_k = \text{grad } F_k == \text{the affinity or driving force.}$$

$$\vec{J}_k = \text{the flux related to } dx_k/dt \text{ by continuity, flows in response to the driving force affinity}$$

$$ds/dt = \vec{f}_k \cdot \vec{J}_k = \text{rate of increase of entropy}$$

[†] critical phenom. binder has more Callan notes.

4. Now we would like to know how the responding fluxes are related to the affinity driving forces which are causing the fluxes. If your system has no "memory" (say in the form of capacitance-like effects), it is called a Markoff process and you may conclude that:

$$J_k = J_k (f_i, F_i)$$

Ie, the fluxes are functions of the forces and their gradients at an instant of time, there is no need to integrate over the past somehow.

In my mind, the state of the parameters F_i just sets the stage, ie, sets the "operating point" of the process, whereas the f_i are the actual driving forces. Clearly J_k will depend more on f_k than on any other force, but we should expect integactions.

Note: J_k is not a function of $U, X_1, X_2 \dots$ the extensive parameters. Should be able to prove this.

5. Now assume that all driving forces are very small in some sense, ie, you are not too far away from equilibrium. Then you treat the flux J_k as a function of two variables and expand in the affinity like so:

$$J_k = L_{jk} f_j + \text{higher order in } f$$

If you simply ignore higher order effects, you are now talking about a linear Markoff process and knowledge of what is going on is now contained in the matrix of coefficients $L_{jk} = L_{jk}(F_n)$. Ie, these things are only functions of the operating point intensive force parameters F_n .

6. Onsager's Theorem says that you don't really have to figure out all of the entries in this L matrix (called Kinetic Coefficients) because the following is true and can be proved from fluctuation theory:

$$L_{ab}(F_k) = L_{ba}(\text{time reversed } F_k)$$

For example, an external magnetic field would be reversed in such a relationship. Thus, you need to find the diagonal entries of L and one side only.

7. Simplest possible example of the linear Markoff application: Let $X_o = U$ and then $F_o = (1/T)$ so that $f_o = \text{grad}(1/T)$. Suppose there are no other intensive parameters in the problem. The flux J_o is of course a "total energy flux" which shows how energy flows in response to a temperature gradient. Your L matrix has only one entry (for isotropic material, I guess):

$$J_o = L_{oo} \text{ grad}(1/T) = [-L_{oo}/T^2] \text{ grad}(T).$$

Thus you would identify $L_{oo} = \text{Kappa} \times T^2$ where kappa is the usual thermal conductivity that you look up in tables for some material. Ohm's Law is another example.

8. The general philosophy of using these "Onsager Equations" is to try and identify all the L_{ij} coefficients with known system parameters, then you will get a system of coupled linear equations which describe what happens! And all coefficients are known.

Notice that, as is always the case in thermo, we never have any method for computing any of these constants. Thermo gives us correlations between things, but does not explain on the micro-level what is actually happening. Ie, we might like to know exactly how the affinity creates the flux and so on.

ThermoElectric Effects

We are now going to apply all of the above formalism to a system with basically only two intensive parameters:

$$\begin{aligned} x_0 &= u = \text{the total energy density} & F_0 &= (1/T) \\ x_1 &= n \text{ the electron density} & F_1 &= (-u/T) \end{aligned}$$

Here, μ is the electrochemical potential of a single electron. Recall that this is somehow the force felt by the electron. We know that such a force has a drift part related to electric fields and potentials, and a diffusion part related to density gradients. Both electric fields and density gradients can "push" an electron around, so they both contribute to the potential μ .

Our opening equation (the first law in entropy rep) says:

$$ds = (1/T) du - (\mu/T) dn$$

Obviously we have various kinds of fluxes: J_u = flux of total energy
 (J_s related to J_u and J_n by the above) J_n = flux of electrons
 J_s = flux of total entropy

Of course we can also write the first law as $du = Tds + (\mu) dn = dq + (\mu) dn$ so we can introduce J_Q = a heat current related to J_u and J_n as shown.

Actually, the electric current eJ_n and the heat current J_Q are the two that are most interesting to us physically, so we choose them as our basic flux variables.

Affinity associated with $x_2 = q$ is $F_2 = (ds/dq) = (1/T)$, so $f_2 = \text{grad}(1/T)$
 Affinity associated with $x_1 = -n$ is $F_1 = (\mu)/T$ so $f_1 = \text{grad}(\mu/T)$

However, this point of view is not quite valid because heat is not really an ~~intensive~~ extensive variable. ? Well maybe it is OK . When we do $\text{grad}(\mu/T)$ however we can combine the term $(\mu) \text{grad}(1/T)$ with the second term and redefine the L's. Thus you get:

$$\begin{aligned} -J_n &= L_{11} [(1/T) \text{grad}(\mu)] & + & L_{12} [\text{grad}(1/T)] \\ J_Q &= L_{21} [(1/T) \text{grad}(\mu)] & + & L_{22} [\text{grad}(1/T)] \end{aligned}$$

Here we see that thermo-electric effects (effects involving heat and electric currents) are most simply modeled as a two-dimensional linear Markov process!

The next step is to try and identify the various coefficients!

1. Now, here is how you identify L_{11} and L_{22} with known constants; .

(a) Consider an electric current through a wire at constant temperature. The $\text{grad}(1/T)$ terms in the Markoff equations thus vanish. If $n = n(T)$, then there will be no density gradient, so the chemical μ_c has no gradient, and only the electrical μ_e has a gradient which is of course the electric field. In this way you can quickly relate L_{11} to the conductivity parameter sigma.

(b) Now suppose you have a temperature gradient and a heat current through a wire, but no electric current. You cannot in this case set any terms equal to zero in the Markov equations, but you can invert them as a 2×2 matrix equation (in effect eliminating the unknown $\text{grad}(\mu)$ to relate the thermal conductivity kappa to the three L's. Note that $\text{kappa} \neq f(L_{22})$ only.

In doing this matrix inversion, we also get a special equation (17.24) which is of course valid only when there is no electric current.

2. There is still one unknown parameter which we have to figure out how to measure. Let us define:

$$\epsilon = -L_{12}/(eTL_{11})$$

This you see is essentially the parameter that appears in that equation (17.24) which applies when no currents. If you integrate this equation around a standard thermocouple, you find:

$$V_{\text{Seebeck}} = \int_{T_1}^{T_2} [\epsilon_B - \epsilon_A] dT$$

or

$$dV/dT = (\epsilon_B - \epsilon_A) = \text{"the thermoelectric power of thermocouple"}$$

Note: While measuring this thermocouple voltage, we must make sure no current is drawn, otherwise we invalidate using (17.24). This voltage measurement with no current is called the Seebeck Effect or Seebeck voltage.

Note: although the absolute thermoelectric power ϵ clearly exists and is calculable from first principles, the Seebeck Effect only allows you to measure relative epsilons. At some point you must know the epsilon for some metal (perhaps platinum), then you can measure the rest. I wonder what experiment lets you measure absolute epsilon?

3. The Peltier Effect. From (17.35), consider a current running through a junction held at constant temperature T. Since no T gradient, you have $J_q = T \epsilon \cdot J_n$. But we know that ϵ is discontinuous through the junction, whereas T and J_n are continuous; thus J_q is discontinuous and heat is emitted or absorbed at the junction. This is the Peltier effect. Note that no mechanism is actually stated for this process. We are only doing thermo.

Equation turns out to be: $J_q^B - J_q^A = \pi_{BA} (eJ_n)$ where $\pi_{BA} = T(\epsilon_B - \epsilon_A)$

Thus, the junction heat current generated in Peltier Effect is proportional to the electric current crammed through the junction (or generated by it!). The Peltier coefficient is trivially related to the difference of the Seebeck Coefficients. Joule heating has been ignored here.

4. Thomson Effect. Now consider a short piece of wire with a temperature difference dT between the ends. This might be a piece of the wire in a thermocouple which connects the two temperature reservoirs. You can show this:

$$\begin{aligned} du/dt &= \text{rate of production of energy at some point} \\ &= \tau \cdot \text{grad}(T) \cdot (eJ_n) + \text{Joule heating} \end{aligned}$$

This says that there is heat created or absorbed (depending on sign of constant τ) in addition to usual I^2R heating, and this extra heat or loss is called the Thomson Heat or Thomson Effect.

You can see that the heat of this effect is proportional to the current in the wire and to the temperature gradient the wire is in. The actual heating or cooling depends on the relative directions of current and temp gradient.

$$\tau = -T (d\epsilon/dT)$$

So this constant is the derivative of the Seebeck coefficient!

5. Numbers. For typical metals, $(\epsilon_{AB}) = 20 \text{ uV/degree}$ which is very small and makes practical refrigeration difficult. For certain semiconductor materials however this number goes up to perhaps 400 uV/deg.

A typical Seebeck thermocouple voltage from metals is perhaps 6 millivolts. Generally, thermocouple devices operate at voltages like this, and relatively high currents like 40 amperes. They are inherently low resistance devices.

6. Other effects

Fourier Conduction refers simply to the fact that, when you try to make a refrigerator with Thomson or Peltier effects, even when you have no electric currents, heat will leak through your material from the hot to the cold, thus hurting your efficiency. Part of the game in thermo design is to find materials which have low Fourier conduction, but high Seebeck coefficient.

Joule Heating. This is just the $EI = I^2R$ heating in a wire of junction.

References:

Callan, HB. Chapters 2, 16, 17

Zemansky, Chapters 9 and 13.

Reif has nothing except comments on Onsager symmetry.

Angrist Direct Energy Conversion book has some stuff.

Callan Chapter 2 : Conditions of Equilibrium.

$U = U(S, \underbrace{V, N_i}_{\text{extensives}})$ The total energy fctn.

$$\left. \begin{aligned} \left(\frac{\partial U}{\partial S}\right)_{V, N_i} &= T & \text{/temp} \\ \left(\frac{\partial U}{\partial V}\right)_{S, N_i} &= -P & \text{/pressure} \\ \left(\frac{\partial U}{\partial N_i}\right)_{S, V, N_{i \neq i}} &= \mu_i & \text{/chem pot.} \end{aligned} \right\} \text{intensives}$$

Thus,

$$dU = \underbrace{T dS}_{\delta Q} - \underbrace{P dV}_{\delta W_m \text{ (mech.)}} + \underbrace{\mu_i dN_i}_{\delta W_c \text{ (chemical)}}$$

More generally,

$$U = U(S, \underbrace{X_1, X_2, \dots, X_t}_{\text{extensives}})$$

$$\left. \begin{aligned} \left(\frac{\partial U}{\partial X_i}\right) &\equiv P_j \\ \left(\frac{\partial U}{\partial S}\right) &\equiv T \end{aligned} \right\} \text{intensives (general)}$$

Then $dU = T dS + \sum_i P_i dX_i$

Equations of State: $\left. \begin{aligned} P_j &= P_j(S, X_i) \\ T &= T(S, X_i) \end{aligned} \right\} \text{you need all of them to know system.}$

This has been the "energy rep".

Let $S = \text{basic instead so}$ all the extensives)
 $U \equiv X_0$ then $S = S(\overbrace{X_0, X_1, \dots, X_t})$

Now let

$\left(\frac{\partial S}{\partial X_i}\right) \equiv F_i$, the intensive params of
the entropy representation.

Thus $F_0 = \left(\frac{\partial S}{\partial U}\right) = \left(\frac{1}{T}\right)$ note famous - sign.

$$F_i = \left(\frac{\partial S}{\partial X_i}\right) = \left(\frac{\partial S}{\partial U}\right) \left(\frac{\partial U}{\partial X_i}\right) = -\left(\frac{1}{T}\right) (P_i) = -P_i/T.$$

So you can work with the P_i or the X_i .

$$dS = \sum F_i dX_i$$

Theorem: shows, by considering a 2-piece system where $U = U^{(1)} + U^{(2)} = \text{fixed}$,
that $dS = 0 \Rightarrow T_1 = T_2$, as usual.

Theorem: by same argument, you show $dS = 0 \Rightarrow P^{(1)} = P^{(2)}$, ie,
mechanical equilibrium also!

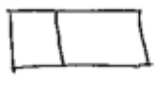
Theorem: similarly, $\mu^{(1)} = \mu^{(2)}$ in T.E.

end of chapter 2, 16 pages.

Callan's Chapter 16 "Irreversible Thermodynamics"

Here we will apply thermo ideas to non-Thermo-equ situations. This is the famous quasi-thermal-equilibrium. In any region, things are very close to TE.

(1) Review the TE mechanical balance idea.

Two systems [ say] so $X_k + X'_k = \text{const.}$
(volumes).

$$dS = F_k dX_k + F'_k dX'_k$$

$$\text{so } dS = 0 \Rightarrow F_k = F'_k.$$

Define:

$$\mathcal{F}_k \equiv \left(\frac{\partial S^{\text{tot}}}{\partial X_k} \right) = F_k - F'_k = \text{"affinity"}.$$

The net gen. force, sort of a driving force. In TE, $\mathcal{F}_k \equiv 0$.

Note:

$$\mathcal{F}_0 = \frac{1}{T} - \frac{1}{T'}$$

$$\mathcal{F}_i = -\frac{P_i}{T} + \frac{P'_i}{T'}, \text{ eg.}$$

Imagine near TE and $\mathcal{F}_k \neq 0$. This causes a response (diaphan mouse).

$$J_k \equiv \frac{dX_k}{dt}, = \text{response of system (volume change due to affinity } \neq 0).$$

Note:

$$\frac{dS^{\text{tot}}}{dt} = \frac{dS^{\text{tot}}}{dX_i} \frac{dX_i}{dt} = \boxed{\sum_i F_i J_i = \dot{S}^{\text{tot}}} \quad \leftarrow$$

As system is in the action of adjusting, S increases! !

Next — we want to restate where system of interest is small diff. piece of continuum.

Recall $dS = \sum_k F_k dX_k$

Divide by d^3x volume to say

$$ds = \sum_k F_k (dx_k)$$

eg, dn_k , change in a density.

Now imagine flow densities of entropy and all extensive.

$$0 = \frac{\partial X_k}{\partial t} + \vec{\nabla} \cdot \vec{J}_k$$

/says you cannot create number density a energy density.

$$\dot{s} = \frac{\partial s}{\partial t} + \vec{\nabla} \cdot \vec{J}_s$$

/but you can create entropy!

Now seems reasonable that

$$dS = \sum_k (F_k dX_k) \quad (1)$$

$$\Rightarrow \vec{J}_s = \sum_k (F_k \vec{J}_k) \quad (2)$$

Assume (2), take $\vec{\nabla} \cdot$ to get

$$\begin{aligned} \dot{s} - \frac{\partial s}{\partial t} &= \underbrace{\sum_k F_k \left(-\frac{\partial X_k}{\partial t}\right)}_{= \frac{\partial s}{\partial t}, \text{ the explicit dep.}} + \vec{\nabla} \cdot \vec{J}_s \end{aligned}$$

may vary in space.

Thus:

$$\dot{s} = \sum_k \vec{\nabla} F_k \cdot \vec{J}_k \quad / \text{continuous}$$

Compare.

$$\dot{s} = \sum_k \underbrace{\vec{\nabla} F_k}_{\text{affinity}} \cdot \vec{J}_k \quad / \text{two-part system.}$$

affinity is now gradient of parameter F .

/more chap 16, page 2. $\vec{F}_k$, new affinity.

So

$$\dot{S} = \sum_k \left(\vec{\nabla} F_k \right) \cdot \vec{J}_k$$

example. $F_0 = \frac{1}{T}$, so $\vec{\nabla} F_k = \vec{\nabla} \left(\frac{1}{T} \right) =$ the driving force.
 $\vec{J}_0$ related to $x_0 = u$, the energy current.

So temperature gradient causes response of energy flux.

Markoff System. $\vec{J}_k = \vec{J}_k(\vec{F}_i, F_i)$

→ The "local fluxes" are fctns of local intensities + affinities at same time, no dependence on $\vec{F}$ or F in the past. (else non-Markoffian).

● Suppose small affinities. Then expand:

$$J_k = \underbrace{\sum_j L_{jk} F_j}_{\text{first order}} + \frac{1}{2!} \sum_{ij} L_{ijk} F_i F_j + \dots$$

where clearly

$L_{jk} = f(F_i)$ only.
↑ kinetic coefficients

/response J_k due to force F_j .

Onsager's Theorem

$$L_{jk}(F_i) = L_{kj}(\underbrace{\text{time reversed } F_i}_{-\vec{B}}).$$

↑
eg $\vec{B}$

Related to detailed balance.

If you keep only first order, then

$$\underbrace{J_k}_{\text{flux}} = \sum_j \underbrace{L_{jk}}_{\text{kin. coeff.}} \underbrace{F_j}_{\text{affinity}} = \text{linear Markoff process!}$$

Example: $\vec{F}_0 = \vec{\nabla} \left(\frac{1}{T} \right)$

$$\vec{J}_0 = (L_{00}) \vec{\nabla} \left(\frac{1}{T} \right) = - \underbrace{\left(\frac{L_{00}}{T^2} \right)}_{\text{thermal conductivity} \cdot K} \vec{\nabla} T.$$

Here only one diagonal coeff, L_{00} .

So
$$\vec{J}_0 = \underbrace{(KT^2)}_{L_{00}} \vec{\nabla} \left(\frac{1}{T} \right) = \text{example of our construction.}$$

Idea: Let $\chi_k = \rho$, charge density. Then

$$U = \int \frac{|\vec{E}|^2}{8\pi} \quad \vec{E} = \vec{\nabla} \phi.$$

$$= \int \vec{\nabla} \phi \cdot \vec{\nabla} \rho = \int \rho \cdot \phi \quad \text{so} \quad P = \phi, \text{ then gen func,}$$

and $F = -\frac{\phi}{T}$ and $\vec{F} = -\vec{\nabla} \left(\frac{\phi}{T} \right)$

Then:

$$\begin{aligned} \vec{J} &= L \vec{F} = L \left[-\vec{\nabla} \left(\frac{\phi}{T} \right) \right] \\ &= -L \left[\phi \vec{\nabla} \left(\frac{1}{T} \right) + \frac{1}{T} \vec{\nabla} \phi \right] \\ &= \underbrace{(-L\phi) \vec{\nabla} \left(\frac{1}{T} \right)}_{\text{assume 0.}} + \left(\frac{L}{T} \right) \vec{\nabla} \phi \end{aligned}$$

$\propto$ elect. conduct

Ohm's Law.

Chapter 11: Effects such as Thermoelectrics

Kelvin in 1854 proposed an incomplete theory ~ modern theory was just given in last chapter.

$$ds = \sum_k F_k dx_k = \underbrace{\left(\frac{1}{T}\right)}_{F_0} du + \underbrace{\left(-\frac{\mu}{T}\right)}_{F_1} dn \quad / \text{ignore enthalpy of atomic ions, etc.}$$

$$\begin{cases} F_0 = \left(\frac{1}{T}\right) \\ x_0 = u = \text{energy density.} \end{cases}$$

$$F_1 = -\frac{\mu_1}{T} \quad \text{where} \quad \mu_1 = \left(\frac{\partial \psi}{\partial n_1}\right)_S = \text{electron's potential}$$

$$x_1 = n_1 = \text{electron density}$$

Now

$$\vec{J}_s = \underbrace{\left(\frac{1}{T}\right)}_{F_0} \underbrace{\vec{J}_u}_{\text{energy flux}} + \underbrace{\left(-\frac{\mu}{T}\right)}_{F_1} \underbrace{\vec{J}_n}_{\text{electron flux}} \quad / \text{from our general formula. (17.2)}$$

Also,

$$\dot{S} = \underbrace{\vec{\nabla}\left(\frac{1}{T}\right)}_{\vec{F}_0}_{\text{energy affinity}} \cdot \vec{J}_u + \underbrace{\vec{\nabla}\left(-\frac{\mu}{T}\right)}_{\vec{F}_1} \cdot \vec{J}_n \quad (17.3)$$

Linear Markov says:

$$\begin{aligned} \vec{J}_u &= L_{uu} \vec{\nabla}\left(\frac{1}{T}\right) + L_{un} \vec{\nabla}\left(-\frac{\mu}{T}\right) \\ \vec{J}_n &= L_{un} \vec{\nabla}\left(\frac{1}{T}\right) + L_{nn} \vec{\nabla}\left(-\frac{\mu}{T}\right). \end{aligned}$$

This really assumes one-dim.

General Markov sz

$$\vec{J}_k = \sum_j [L_{jk}] \vec{F}_j$$

so in general each L_{jk} is a 3×3 matrix (tensor).
But if all confined to one dim (as in a thin wire),
then

$$\begin{aligned} (J_k)_i &= \sum_{\ell j} [L_{\ell k}]_{ij} [F_{\ell}]_j \\ &\approx \sum_{\ell} (L_{\ell k})_{ii} (F_{\ell})_i \end{aligned}$$

i.e., ignore all lateral effects. Then I accept:

$$\begin{aligned} -J_N &= L'_{11} \nabla \left(\frac{\mu}{T} \right) + L'_{12} \nabla \left(\frac{1}{T} \right) \\ +J_u &= L'_{21} \nabla \left(\frac{\mu}{T} \right) + L'_{22} \nabla \left(\frac{1}{T} \right). \end{aligned}$$

Compare to my earlier:

So

$$L'_{12} (\vec{H}) = L'_{21} (-\vec{H})$$

Time reverse idea.

Proven.

$$L'_{11} = L_{nn}$$

$$\begin{pmatrix} L'_{12} = -L_{nn} \\ L'_{21} = -L_{nn} \end{pmatrix}$$

$$L'_{22} = L_{uu}$$

/ chap 17, page 2.

$$dU = TdS + \mu dN = dQ + \mu dN \Rightarrow \vec{J}_U = \vec{J}_Q + \mu \vec{J}_N$$

$\uparrow$ total energy current $\uparrow$ heat current.

Replace $\vec{J}_U$ by $\vec{J}_Q$ in (17.3)

$$\dot{S} = \vec{\nabla} \left(\frac{1}{T} \right) \cdot \vec{J}_Q + \underbrace{\vec{\nabla} \left(\frac{1}{T} \right) \cdot \mu \vec{J}_N - \vec{\nabla} \left(\frac{\mu}{T} \right) \cdot \vec{J}_N}_{-\frac{1}{T} \vec{\nabla} \mu \cdot \vec{J}_N} \quad (17.9)$$

So reinterpret

$$\dot{S} = \underbrace{\vec{\nabla} \left(\frac{1}{T} \right)}_{\uparrow} \cdot \vec{J}_Q + \underbrace{\left[+\frac{1}{T} \vec{\nabla} \mu \right]}_{\uparrow} \cdot (-\vec{J}_N)$$

new affinity.

Then linear Markov steps.

$$\begin{aligned} (-\vec{J}_N) &= L_{11} \cdot \left[\frac{1}{T} \vec{\nabla} \mu \right] + L_{12} \left[\vec{\nabla} \left(\frac{1}{T} \right) \right] \\ (\vec{J}_Q) &= L_{21} \cdot \left[\frac{1}{T} \vec{\nabla} \mu \right] + L_{22} \left[\vec{\nabla} \left(\frac{1}{T} \right) \right]. \end{aligned}$$

we just did a slight shuffle.

Note: $\mu \vec{J}_N = (\text{potential per particle [electrons]}) \times \vec{J}_N = \text{"pot. energy current"}$.

17.2 Now consider a wire with both heat and electrical current.

$$\mu = \underbrace{\mu_e + \mu_c}_{e\phi}$$

$$\vec{\nabla} \mu = \underbrace{-e \vec{E}}_{\substack{\text{electric} \\ \text{drift} \\ \text{force}}} + \underbrace{\vec{\nabla} \mu_c}_{\substack{\text{concentration gradient,} \\ \text{the "force" of diffusion}}}$$

$$\sigma = \frac{L_{11} e^2}{T}$$

Consider homogen system ($\mu_c = \text{const}$) so then $-\vec{J}_N = \frac{L_{11}}{T} [-e \vec{E}]$

isothermal

So we now know that $\sigma = \frac{e^2 L_{11}}{T}$, we can relate L_{11} to normal electric conduct. (17.20)

Now consider a situation with $J_Q \neq 0$ by $J_V = 0$ then.

$$K \equiv -\frac{J_Q}{\nabla T} \quad \text{but} \quad J_V = 0 \Rightarrow L_{11} \frac{1}{T} \vec{\nabla} \mu + L_{12} \vec{\nabla} \left(\frac{1}{T} \right) = 0.$$

So write:

$$\begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} \frac{1}{T} \vec{\nabla} \mu \\ \vec{\nabla} \left(\frac{1}{T} \right) \end{pmatrix} = \begin{pmatrix} -J_V \\ J_Q \end{pmatrix} = \begin{pmatrix} 0 \\ -K \vec{\nabla} T \end{pmatrix}$$

Then:

$$\begin{bmatrix} \frac{1}{T} \vec{\nabla} \mu \\ \frac{1}{T^2} \vec{\nabla} T \end{bmatrix} = \frac{1}{D} \begin{bmatrix} L_{22} & -L_{12} \\ -L_{21} & L_{11} \end{bmatrix} \begin{bmatrix} 0 \\ -K \vec{\nabla} T \end{bmatrix}$$

Thus

$$\frac{1}{T} \vec{\nabla} \mu = \frac{1}{D} K L_{12} \vec{\nabla} T$$

$$-\frac{1}{T^2} \vec{\nabla} T = -\frac{1}{D} K L_{11} \vec{\nabla} T \Rightarrow \frac{1}{T^2} = \frac{K L_{11}}{D} \Rightarrow K = \frac{D}{T^2 L_{11}} \quad (17.22)$$

Then this we say

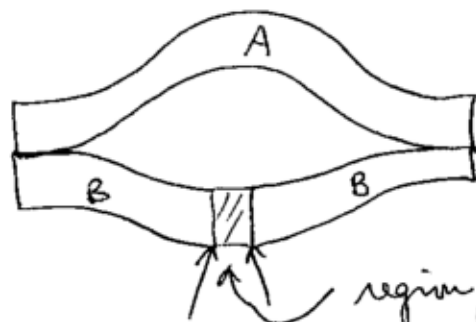
$$\vec{\nabla} \mu = \frac{T K L_{12}}{D} \vec{\nabla} T = \frac{T D}{T^2 L_{11} D} L_{12} \vec{\nabla} T = \left(\frac{L_{12}}{T L_{11}} \right) \vec{\nabla} T = \vec{\nabla} \mu \quad (17.24).$$

So, we have made some connection

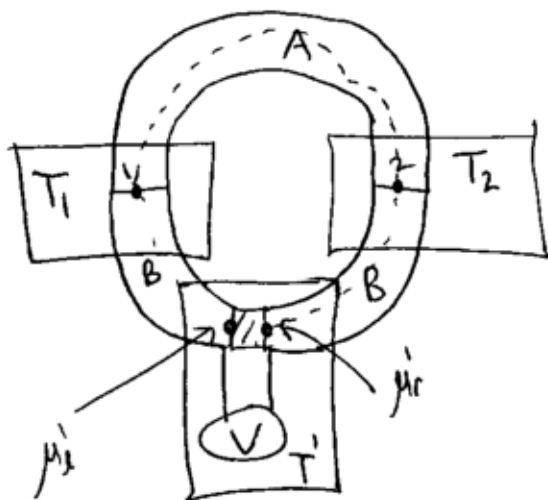
$$\sigma = \frac{e^2 L_{11}}{T} \quad \text{where} \quad (e \vec{J}_V) = \sigma \vec{E}$$

$$K = \frac{L_{11} L_{22} - L_{12}^2}{T^2 L_{11}} \quad \text{where} \quad \vec{J}_Q = -K \vec{\nabla} T$$

There is still another parameter in here!



region passes heat, but blocks current.



Integrate (17.24) to get:

$$\mu_2 - \mu_1 = \int_1^2 \frac{L_{12}^A}{T L_{11}^A} dT$$

$$\mu_2' - \mu_2 = \int_2^r \frac{L_{12}^B}{T L_{11}^B} dT.$$

$$\mu_1 - \mu_1' = \int_r^1 \frac{L_{12}^B}{T L_{11}^B} dT.$$

$$\mu = \mu$$

/note. At points $2+\epsilon, 2-\epsilon$ $\mu = \mu_2$, i.e., $\mu^\pm = \mu_2$ due to T.E.!

/But $\mu_2' \neq \mu_2$ because ^{elec} current is not free to flow!

/note: voltmeter reads $\mu_2' - \mu_1'$ because $\mu_2'(\text{chem}) = \mu_1'(\text{chem})$.

These are equal because. $\mu_{\text{chem}} = f(T, n)$ and materials are same and at same T!

So:

$$\mu_2' - \mu_1' = eV = \int_1^2 \frac{L_{12}^A}{T L_{11}^A} dT + \int_2^1 \frac{L_{12}^B}{T L_{11}^B} dT$$

But leads are continuous then the isothermal cut, so

$$eV_{\text{Seebeck}} = \int_{T_1}^{T_2} \left[\frac{L_{12}^A}{L_{11}^A} - \frac{L_{12}^B}{L_{11}^B} \right] \frac{dT}{T} \quad (17.29).$$

This says: if $T_1 \neq T_2$, $\left\{ \begin{array}{l} \text{seebeck coefficient} \\ \text{you develop an emf!} \end{array} \right.$

Now define:

$$\epsilon = -\frac{L_{12}}{eTL_{11}}$$

= absolute
thermo electric
power.

Then our params are σ, K, ϵ and

$$V = \int_1^2 (\epsilon_B - \epsilon_A) dT$$

$$\Rightarrow \left(\frac{\partial V}{\partial T_2} \right) = \epsilon_B - \epsilon_A \equiv \epsilon_{AB} = \text{thermoelectric power of thermocouple.}$$

in perhaps mV/degree.

So go back + replace:

$$L_{11} = \left(\frac{T\sigma}{e^2} \right)$$

$$\left(\frac{-L_{12}}{L_{11}} \right) = eT\epsilon$$

$$L_{12} = \frac{KT^2}{1+eT\epsilon}$$

$$K = \frac{1}{T^2} \left[L_{22} - \frac{L_{12}^2}{L_{11}} \right]$$

$$K = \frac{L_{12}}{T^2} \left[\frac{L_{22}}{L_{12}} - \frac{L_{12}}{L_{11}} \right]$$

$$= \frac{L_{12}}{T^2} \left[\frac{L_{22}}{L_{12}} - eT\epsilon \right]$$

Stop: $L_{11} = \frac{T\sigma}{e^2}$

$$L_{12} = -eTL_{11}\epsilon = -eT\epsilon \frac{T\sigma}{e^2} = -\frac{T^2\sigma\epsilon}{e}$$

/chap 17, page 4

Then $KT^2 L_{11} = L_{11} L_{22} - L_{12}^2$

so $KT^2 + \frac{L_{12}^2}{L_{11}} = L_{22} = KT^2 + \frac{[T^4 \epsilon^2 \sigma^2 / e^2]}{T \sigma / e^2}$

$\Rightarrow L_{22} = KT^2 + T^3 \sigma \epsilon^2$

So, $-\vec{J}_N = \overbrace{\left(\frac{T \sigma}{e^2}\right)^{-1}}^{L_{11}} \nabla \mu + \overbrace{\left(-\frac{T^2 \epsilon \sigma}{e}\right)}^{L_{12}} \nabla \left(\frac{1}{T}\right)$ (17.33)

$\vec{J}_Q = \underbrace{\left(-\frac{T^2 \epsilon \sigma}{e}\right)^{-1}}_{L_{12}} \nabla \mu + \underbrace{(KT^2 + T^3 \sigma \epsilon^2)}_{L_{22}} \nabla \left(\frac{1}{T}\right)$ (17.34)

We have just restated our linear Markov equations.

$\vec{J}_S = \frac{1}{T} \vec{J}_Q$

Go way back + recall

$\dot{S} = \vec{\nabla} \left(\frac{1}{T}\right) \cdot T \vec{J}_S - \frac{1}{T} \vec{\nabla} \mu \cdot \vec{J}_N$ / for later use.

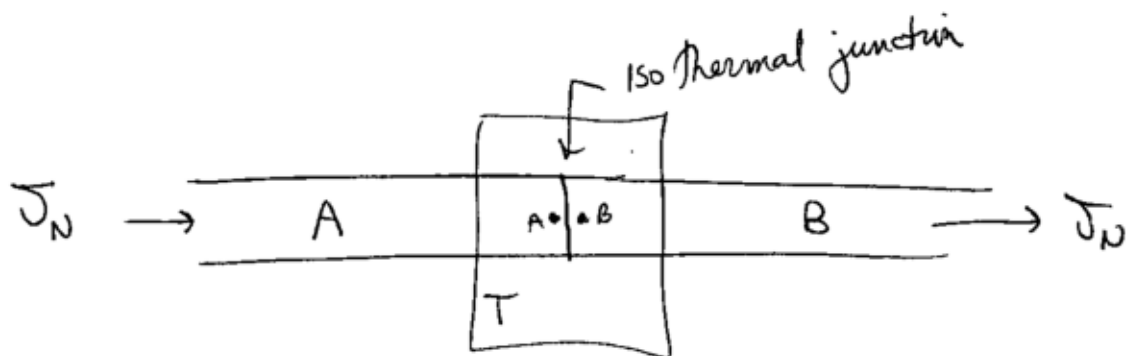
Also

$\vec{J}_S = \underbrace{\epsilon (e \vec{J}_N)}_{\text{entropy current with no electric current.}} + \underbrace{TK \vec{\nabla} \left(\frac{1}{T}\right)}_{\text{extra entropy current. Each electron carries } (\epsilon e) \text{ worth of entropy.}}$

Also, note

$\vec{J}_Q = (T \epsilon e) \vec{J}_N + KT^2 \vec{\nabla} \left(\frac{1}{T}\right)$ (17.35)

17.4 The Peltier Effect



Run an electric current thru junction. From (17.35) we have:

$$\vec{J}_{Q,A} = (eTE_A) \vec{J}_{N,A}$$

$$\vec{J}_{Q,B} = (eTE_B) \vec{J}_{N,B}$$

since $\vec{\nabla}(\frac{1}{T}) = 0$ [junction is isothermal].

But clearly $\vec{J}_{N,A} = \vec{J}_{N,B}$, cons. of charge. So

$$J_Q^B - J_Q^A = \underbrace{eT(\epsilon_B - \epsilon_A)}_{\equiv \pi_{AB}, \text{ the Peltier Coeff.}} \vec{J}_N$$

This says there must be a heat flow into environment at this junction, driven by the electric current!

Clearly $\pi_{AB} = T \cdot \epsilon_{AB} \leftarrow \text{"second Kelvin relation" (17.40).}$

$\uparrow$ Peltier $\uparrow$ thermopower.

Thus, you can heat a cool in this way!!

17.5 The Thomson Effect.

/preliminary calc:

$$\vec{\nabla} \cdot \vec{J}_u = \vec{\nabla} \cdot [\vec{J}_q + \mu \vec{J}_N] \quad \text{since } dU = dQ + \mu dN.$$

$$= (\vec{\nabla} \cdot \vec{J}_q) + \underbrace{\vec{\nabla} \mu \cdot \vec{J}_N}_{\substack{\text{use (17.33) to get}}} \quad \text{since } \vec{\nabla} \cdot \vec{J}_N = 0 \text{ in a wire.}$$

$$\vec{\nabla} \mu = \left[-\vec{J}_N \cdot \frac{e^2}{\sigma} + eT^2 \vec{\nabla} \left(\frac{1}{T} \right) \right]$$

use (17.35) to get $\vec{\nabla} \cdot [T^2 e \vec{J}_N + T^2 K \vec{\nabla} \left(\frac{1}{T} \right)]$.

hence (17.42), hence (17.43)

$$\vec{\nabla} \cdot \vec{J}_u = T \vec{\nabla} \epsilon \cdot (e \vec{J}_N) + \vec{\nabla} \cdot (T^2 K \vec{\nabla} \left(\frac{1}{T} \right)) - \frac{e^2}{\sigma} \vec{J}_N^2$$

Physical: imagine a wire with $\vec{J}_N = 0$ in steady state.

This means $i = 0$ so $\vec{\nabla} \cdot (T^2 K \vec{\nabla} \left(\frac{1}{T} \right)) = 0$ + this with BC's will determine T distribution.

Now assume that your wire is forced to hold this T distribution by continuous set of reservoirs. Now jam thru a current $\vec{J}_N$. Then.

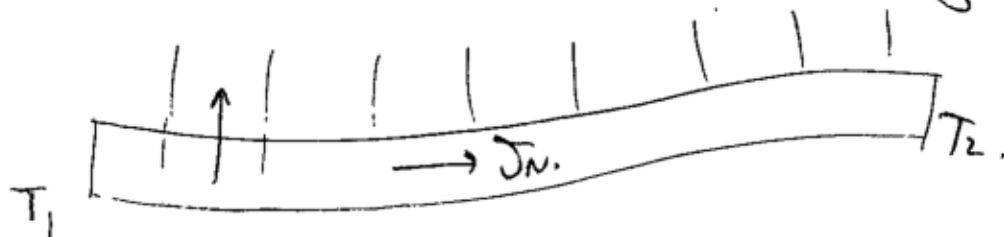
$$\vec{\nabla} \cdot \vec{J}_u = T \underbrace{\vec{\nabla} \epsilon \cdot (e \vec{J}_N)}_{\substack{\text{since second term still vanishes}}} - \frac{1}{\sigma} (e \vec{J}_N)^2 = i$$

since second term still vanishes $\quad \quad \quad = \vec{\nabla} \epsilon(T) = \frac{\partial \epsilon}{\partial T} \vec{\nabla} T$

So we get $\underbrace{\quad}_{\equiv \mathcal{Z}^2, \text{ Thomson coefficient.}}$

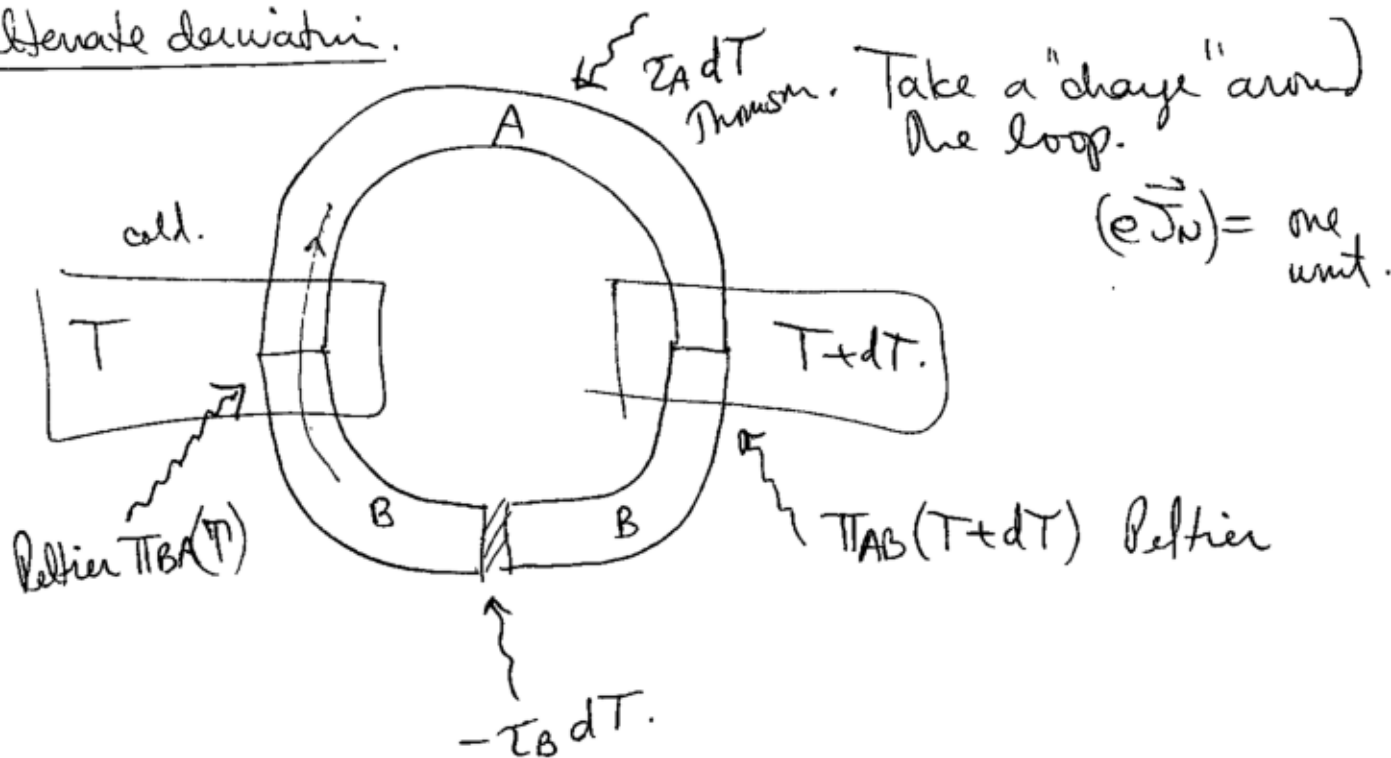
$$\mathcal{Z} \equiv -T \frac{d\epsilon}{dT}$$

$$\dot{u} = \underbrace{-T \left(\frac{d\epsilon}{dT} \right) \vec{\nabla} T \cdot (e \vec{J}_N)}_{\text{Thomson heat!}} + \underbrace{\frac{1}{\sigma} (e \vec{J}_N)^2}_{\text{just } I^2 R \text{ energy generation "Joule heating"}}$$



Into each reservoir is dumped Joule heat + Thomson heat.

Alternate derivation.



In each wire you have a Thomson heat effect.

At each join you have a Peltier heat effect.

So,

/chap 17, page 6.

So total work ~~done~~ taking charge slowly around loop is
heat absorbed

$$\pi_B(T) + \tau_A dT + \pi_{AB}(T+dT) + \tau_B(-dT) = -(\epsilon_B - \epsilon_A) dT$$

But you must get same result traversing thru battery which is balancing the Peltier voltage, so.

$$dV = (\epsilon_B - \epsilon_A) dT$$

$$\Rightarrow \frac{\pi_{AB}(T+dT) - \pi_{AB}(T)}{dT} + (\tau_A - \tau_B) dT = (\epsilon_A - \epsilon_B) dT$$

$$\Rightarrow \boxed{\frac{d\pi_{AB}}{dT} + (\tau_A - \tau_B) = (\epsilon_B - \epsilon_A)} \leftarrow \text{"just Kelvin relation"}$$

But $\pi_{AB} = T(\epsilon_B - \epsilon_A)$ so

$$(\epsilon_B - \epsilon_A) + T \frac{d\epsilon_B}{dT} - T \frac{d\epsilon_A}{dT} + \tau_A - \tau_B = \epsilon_B - \epsilon_A$$

$= 0.$

OK. This rederives $\tau_A = T \left(\frac{d\epsilon_A}{dT} \right).$

/stop. Rest of chapter is thermo-magnetic effects.

Lomansky $\tau_A = " \sigma_A "$.

$$(13.22) \text{ says } \frac{\sigma_A - \sigma_B}{T} = - \frac{d}{dT} \left[\frac{\pi_{AB}}{T} \right]$$

$$= - \left[T \frac{d\pi_{AB}}{dT} - \pi_{AB} \cdot 1 \right] \frac{1}{T^2}$$

$$= - \frac{1}{T} \frac{d\pi_{AB}}{dT} + \frac{\pi_{AB}}{T^2}$$

$$\Rightarrow \sigma_A - \sigma_B = - \frac{d\pi_{AB}}{dT} + \frac{\pi_{AB}}{T} \quad \epsilon_A - \epsilon_B \Rightarrow \frac{d\pi_{AB}}{dT} + (\sigma_A - \sigma_B) = (\epsilon_A - \epsilon_B).$$

Review:

Peltier: → current is driven through an isothermal junction

⇒ heat absorbed/emitted

$$\dot{Q} = \pi_{AB} I$$

Thomson: → current is driven through a temp gradient (no jctn.)

⇒ same result.

$$\left(\frac{d\dot{Q}}{dx}\right) = \tau \cdot I \cdot \left(\frac{dT}{dx}\right)$$

heat gain off per length.

temp. grad.

Practical:

Peltier Refrigerator:

$$(\epsilon_{Cu} - \epsilon_{Fe}) = 13.7 \mu V / \text{deg}$$

at 10 couples in series + 20A

+ operate at 270°K (to make ice cubes),

you can only get $\frac{3}{4}$ watt of cooling!

$$\text{Better: } (\epsilon_{Sb} - \epsilon_{Bi}) = 109 \mu V / \text{deg}.$$



1838 Lenz tried to freeze a drop of water.

Fourier conduction + Joule heating hurt you.

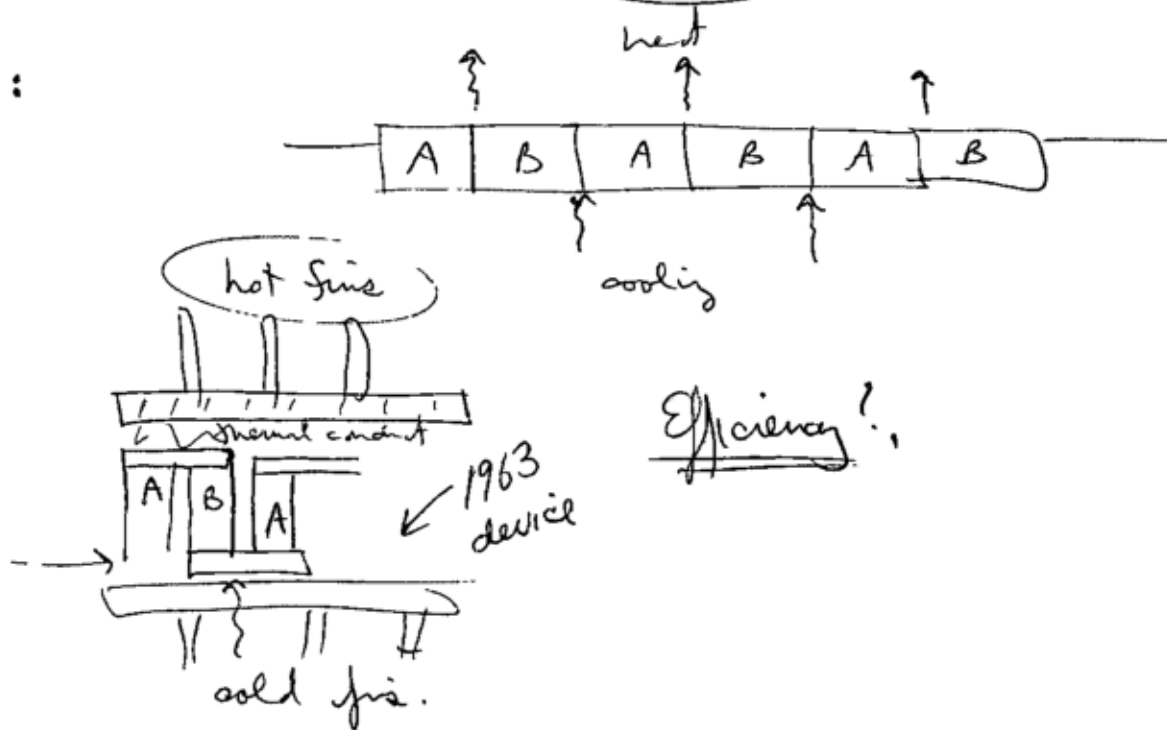
/chap 17, page 9 (really Demanding p 420).

p-type Bi_2Te_3 | n-type same.

$$(\epsilon_A - \epsilon_B) = 423 \mu\text{V}/\text{deg}!$$

10 couples + 20 amps → 23 watts

Design:



Efficiency?

Theoretical Max Efficiency: $\eta(\text{Carnot}) = 1 - \frac{T_c}{T_H}$ (engine)
 = 100% only if $T_c = 0^\circ\text{K}$.

$T_2 = \text{cold}$
 $T_1 = \text{ambient}$

$$W(\text{min}) = T_1 (S_1 - S_2) - Q$$

$$-Q_{\text{max}} = T_1 (S_1 - S_2) + W$$

↑ cooling effect

must do more work.

$$\text{so } \frac{-Q}{W} = 1 + \left(\frac{T_1 (S_2 - S_1)}{W} \right)$$

can be 10.

Lemansky page 437 problem 13-14.

// numbers

$$(\epsilon_{Bi} - \epsilon_{Pb}) = \underbrace{-43.7 \mu V / \text{deg}}_{\text{value at } T = 0^\circ C} - 0.47 \frac{\mu V}{\text{deg}^2} \cdot T (\text{celcius}).$$
$$= a + bT$$

(a) Thermocouple 0° to $100^\circ C$:

$$E_{AB} = \int_{0^\circ C}^{100^\circ C} [a + bT] dT = a \Delta T + \frac{1}{2} b (T_f^2 - T_i^2).$$

$$= -43.7 \frac{\mu V}{\text{deg}} \times 100 \text{ deg} - \frac{1}{2} (0.47) (100)^2$$

$$= -4370 \mu V - \frac{1}{2} 4700 \mu V$$

$$= -6720 \mu V = \underline{\underline{-6.72 \text{ millivolts}}}$$

(b) at $100^\circ C$ the Peltier coeff is

$$\pi_{AB} = 100^\circ C (a + b \cdot 100^\circ C) = -4370 \mu V - 4700 \mu V$$
$$= -9070 \mu V = \underline{\underline{-9.07 \text{ mV}}}.$$

Then,

$$I_Q = \pi_{AB} \cdot I = -9.07 \text{ mV} \cdot 10 \text{ amps} \approx -91 \text{ mW}.$$

So $\approx \frac{1}{10}$ watt is involved at 10 amps. If these numbers are typical, you need 100 AMPS before you'll feel any effect.

THERMODYNAMICS

an introduction to the
physical theories of equilibrium thermostatics
and irreversible thermodynamics

JOHN WILEY & SONS, INC.

New York • London • Sydney

HERBERT B. CALLEN

Professor of Physics
University of Pennsylvania

sions of the thermodynamic method have been made outside the domain of equilibrium. The associated theory is generally referred to as irreversible thermodynamics or the theory of irreversible processes. It seems probable that this new extension of the theory will provide some of the most significant rewards of the thermodynamic method. Some results of the theory of irreversible thermodynamics are presented in the final chapters of this book.

Philadelphia, Pennsylvania
November 1959

HERBERT B. CALLEN

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1.7-4. A small paddle wheel is installed in the system of problem 1.7-3. The shaft of the paddle wheel extends through the walls of the system and can be driven at 240 rps by an external motor. The viscous torque on the paddle wheel is then 10^4 cm-dynes. If the motor is thus permitted to do work on the system while the volume is kept constant and the system is adiabatically enclosed, the pressure is found to increase at a rate

$$\frac{dP}{dt} = \frac{2}{3V} T\omega$$

where T is the viscous torque and ω is the angular velocity of the paddle wheel.

Using the foregoing process and the process of adiabatic expansion described in problem 1.7-3, find the internal energy of any equilibrium state with arbitrary pressure P and volume V . Choose the state A ($P = 32$ atm, $V = 1$ liter) as the fiducial state.

What are the heat fluxes in each separate step of process a in problem 1.7-3? In each step of process c ?

Answer: Heat flux in the first step of process $a = 560$ liter-atm.

1.7-5. Two moles of a particular single-component system are found to have a dependence of internal energy U on pressure and volume given by

$$U = APV^2 \quad (\text{for } N = 2)$$

where $A = 10 \text{ cm}^{-3}$. Note that doubling the system doubles the volume, energy, and mole number but leaves the pressure unaltered, and write the complete dependence of U on P , V , and N for arbitrary mole number.

Answer: $U = BPV^2/N$, $B = 20/\text{cm}^3$.

1.7-6. Assuming the system of problems 1.7-3 and 1.7-4 to have been a single-component system, show that the complete functional dependence of U on P , V , and N is, in fact, independent of N .

1.7-7. A particular single-component system of one mole has adiabats of the form $PV^{3/2} = \text{constant}$. It is fitted with a stirrer, as in problem 1.7-4. When the stirrer does an amount of work, dW , the pressure increase dP (at constant volume) is given by

$$dW = \left(\frac{3}{2}V + V^{3/2}\right) dP$$

Find the internal energy as a function of P , V , and N .

1.7-8. Show that if a single-component system is such that PV^k is constant in an adiabatic process (k is a positive constant) the energy is

$$U = \frac{1}{k-1} PV + Nf(PV^k/N^k)$$

where f is an arbitrary function.

Hint: First show that $U - \frac{1}{k-1} PV$ is constant on each adiabat.

1.8 The Basic Problem of Thermodynamics

In terms of the definitions and discussions of the preceding sections we are now able to formulate the basic problem of thermodynamics. We

shall find that the mere statement of the problem suggests the postulates which provide its solution.

Let us suppose that two simple systems are contained within a closed cylinder, separated from each other by an internal piston. Assume that the cylinder walls and the piston are rigid, impermeable to matter, and adiabatic and that the position of the piston is firmly fixed. Each of the systems is closed. If we now free the piston, it will, in general, seek some new position. Similarly, if the adiabatic coating is stripped from the piston so that heat can flow between the two systems, there will be a redistribution of energy between the two systems. Again, if holes are punched in

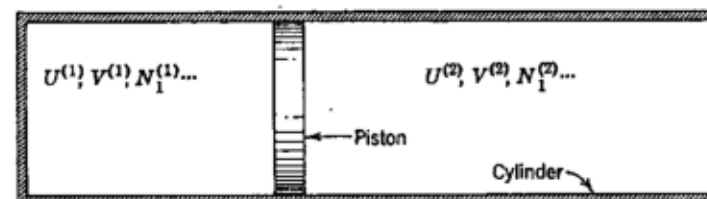


Figure 1.3

the piston, there will be a redistribution of matter (and also of energy) between the two systems. Thus the removal of a constraint in each case results in the onset of some spontaneous process, and when the systems finally settle into new equilibrium states they do so with new values of the parameters $U^{(1)}$, $V^{(1)}$, $N_1^{(1)}$, ... and $U^{(2)}$, $V^{(2)}$, $N_1^{(2)}$, ... The basic problem of thermodynamics is the calculation of the equilibrium values of these parameters.

Before formulating the postulate that provides the means of solution of this problem, we rephrase the problem in a slightly more general form without reference to such special devices as cylinders and pistons.

Given two or more simple systems, they may be considered as constituting a single *composite* system. The composite system is termed closed if it is surrounded by a wall that is restrictive with respect to the total energy, the total volume, and the total mole numbers of each component of the composite system. The individual simple systems within a closed composite system need not themselves be closed. Thus, in the particular example referred to, the composite system is closed even if the internal piston is free to move or has holes in it. Constraints that prevent the flow of energy, volume, or matter among the simple systems constituting the composite system are known as *internal* constraints. If a closed composite system is in equilibrium with respect to certain internal constraints and if some of these constraints are then removed, the system

eventually comes into a new equilibrium state. That is, certain processes which were previously disallowed become allowed or, in the terminology of mechanics, become *virtual* processes. *The basic problem of thermodynamics is the determination of the equilibrium state that eventually results after the removal of internal constraints in a closed composite system.*

1.9 The Entropy Maximum Postulates

The induction from experimental observation of the central principle that provides the solution of our basic problem is by no means straightforward. The logical deviousness of the historical method is matched by the subtlety of the elegant modern quantum statistical approach. Rather than attempting to induce the solution from experiment or deriving it from quantum statistical theory, we therefore merely adopt it as a postulate, depending upon a posteriori rather than a priori justification. But even by this method we shall see that our postulate is not unmotivated; it appears as the most natural and plausible guess that we might make. That is, the postulates that we now adopt provide the *simplest conceivable formal solution* to our basic problem. On this basis alone the problem *might* have been solved; the tentative postulation of the simplest formal solution of a problem is a conventional and frequently successful mode of procedure in theoretical physics.

What then is the simplest criterion that can reasonably be imagined for the determination of the final equilibrium state? From our experience with many physical theories we might expect that the most economical form for the equilibrium criterion is in terms of an extremum principle. That is, we might hope that the values of the extensive parameters in the final equilibrium state are simply those that maximize* some function. And, straining our optimism to the limit, we might hope that this hypothetical function has several particular simple mathematical properties, designed to guarantee simplicity of the derived theory. We develop this proposed solution in a series of postulates.

Postulate II. *There exists a function (called the entropy S) of the extensive parameters of any composite system, defined for all equilibrium states and having the following property. The values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.*

* Or minimize the function, this being purely a matter of convention in the choice of the sign of the function, having no consequence whatever in the logical structure of the theory.

It must be stressed that we postulate the existence of the entropy only for equilibrium states, and that our postulate makes no reference whatsoever to nonequilibrium states. In the absence of a constraint the system is free to select any one of a number of states, *each of which might also be realized in the presence of a suitable constraint.* The entropy of each of these constrained equilibrium states is definite, and the entropy is largest in some particular state of the set. In the absence of the constraint it is this state of maximum entropy that is selected by the system.

In the case of two systems separated by a diathermal wall we may wish to predict the manner in which the total energy U distributes between the two systems. We then consider the composite system with the internal diathermal wall replaced by an adiabatic wall and with particular values of $U^{(1)}$ and $U^{(2)}$ (consistent, of course, with the restriction that $U^{(1)} + U^{(2)} = U$). For each such constrained equilibrium state there is an entropy of the composite system, and for some particular values of $U^{(1)}$ and $U^{(2)}$ this entropy is maximum. These, then, are the values of $U^{(1)}$ and $U^{(2)}$ that obtain in the presence of the diathermal wall, or in the absence of the adiabatic constraint.

All problems in thermodynamics are essentially equivalent to the basic problem we formulated in section 1.8. But the basic problem can be completely solved with the aid of the extremum principle if the entropy of the system is known as a function of the extensive parameters. The relation that gives the entropy as a function of the extensive parameters is known as a *fundamental relation*. It therefore follows that *if the fundamental relation of a particular system is known all conceivable thermodynamic information about the system is ascertainable therefrom.*

The importance of the foregoing statement cannot be overemphasized. The information contained in a fundamental relation is all-inclusive—it is equivalent to all conceivable numerical data, to all charts, and to all imaginable types of descriptions of thermodynamic properties. If the fundamental relation of a system is known, there remains not a single thermodynamic attribute that is not completely and precisely determined.

Postulate III. *The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous and differentiable and is a monotonically increasing function of the energy.*

Several mathematical consequences follow immediately. The additivity property states that the entropy S of the composite system is merely the sum of the entropies $S^{(\alpha)}$ of the constituent subsystems:

$$S = \sum_{\alpha} S^{(\alpha)} \quad (1.4)$$

The entropy of each subsystem is a function of the extensive parameters of that subsystem alone

$$S^{(\alpha)} = S^{(\alpha)}(U^{(\alpha)}, V^{(\alpha)}, N_1^{(\alpha)} \dots N_r^{(\alpha)}) \quad (1.5)$$

The additivity property when applied to conceptually distinct (rather than actually physically distinct) subsystems requires the following property. *The entropy of a simple system is a homogeneous first-order function of the extensive parameters.* That is, if all the extensive parameters of a system are multiplied by a constant λ , the entropy is multiplied by this same constant. Or, omitting the superscript (α) ,

$$S(\lambda U, \lambda V, \lambda N_1 \dots \lambda N_r) = \lambda S(U, V, N_1 \dots N_r) \quad (1.6)$$

The monotonic property postulated implies that the partial derivative $(\partial S / \partial U)_{V, N_1, \dots, N_r}$ is a positive quantity,

$$\left(\frac{\partial S}{\partial U} \right)_{V, N_1, \dots, N_r} > 0 \quad (1.7)$$

As the theory develops in subsequent sections, we shall see that the reciprocal of this partial derivative is taken as the definition of the temperature. Thus the temperature is postulated to be nonnegative.*

The continuity, differentiability, and monotonic property imply that the entropy function can be inverted with respect to the energy and that the energy is a single-valued, continuous, and differentiable function of $S, V, N_1 \dots N_r$. The function

$$S = S(U, V, N_1 \dots N_r) \quad (1.8)$$

can be solved uniquely for U in the form

$$U = U(S, V, N_1 \dots N_r) \quad (1.9)$$

Equations 1.8 and 1.9 are alternative forms of the fundamental relation, and each contains *all* thermodynamic information about the system.

We note that the extensivity of the entropy permits us to scale the properties of a system of N moles from the properties of a system of 1 mole. The fundamental equation is subject to the identity

$$S(U, V, N_1, N_2 \dots N_r) = NS(U/N, V/N, N_1/N \dots N_r/N) \quad (1.10)$$

in which we have taken the scale factor λ equal to $1/N \equiv 1/\sum_k N_k$. For a single-component simple system, in particular,

$$S(U, V, N) = NS(U/N, V/N, 1) \quad (1.11)$$

* The possibility of negative values of this derivative (that is, of negative temperatures) has been discussed by N. F. Ramsey, *Phys. Rev.* 103, 20 (1956). Such states can be produced and maintained for short times in certain unique systems. To accommodate their existence requires subtler and more abstract postulates, and in the interest of simplicity we exclude consideration of these very specialized states.

But U/N is the energy per mole, which we denote by u .

$$u \equiv U/N \quad (1.12)$$

Also, V/N is the volume per mole, which we denote by v .

$$v \equiv V/N \quad (1.13)$$

Thus $S(U/N, V/N, 1) \equiv S(u, v, 1)$ is the entropy of a system of a single mole, to be denoted by $s(u, v)$.

$$s(u, v) \equiv S(u, v, 1) \quad (1.14)$$

Equation 1.11 now becomes

$$S(U, V, N) = Ns(u, v) \quad (1.15)$$

Postulate IV. *The entropy of any system vanishes in the state for which $(\partial U / \partial S)_{V, N_1, \dots, N_r} = 0$ (that is, at the zero of temperature)*

This postulate is an extension, due to Planck, of the so-called *Nernst postulate or third law of thermodynamics*. Historically, it was the latest of the postulates to be developed, being inconsistent with classical statistical mechanics and requiring the prior establishment of quantum statistics in order that it could be properly appreciated. The bulk of thermodynamics does not require this postulate, and we make no further reference to it until Chapter 10. Nevertheless, we have chosen to present the postulate at this point to close the postulational basis.

The foregoing postulates are the logical bases of our development of thermodynamics. In the light of these postulates, then, it may be well to reiterate briefly the method of solution of the standard type of thermodynamic problem, as formulated in section 1.8. We are given a composite system and we assume the fundamental equation of each of the constituent systems to be known in principle. These fundamental equations determine the individual entropies of the subsystems when these systems are in equilibrium. If the total composite system is in a constrained equilibrium state, with particular values of the extensive parameters of each constituent system, the total entropy is obtained by addition of the individual entropies. This total entropy is known as a function of the various extensive parameters of the subsystems. By straightforward differentiation, we compute the extrema of the total entropy function, and then, on the basis of the sign of the second derivative, we classify these extrema as minima, maxima, or as horizontal inflections. In an appropriate physical terminology we first find the *equilibrium states* and we then classify them on the basis of *stability*. It should be noted that in the adoption of this conventional terminology we augment our previous

definition of equilibrium; that which was previously termed equilibrium is now termed *stable equilibrium*, whereas *unstable equilibrium* states are newly defined in terms of extrema other than maxima.

It is perhaps appropriate at this point to acknowledge that although all applications of thermodynamics are equivalent in principle to the procedure outlined there are several alternative procedures that frequently prove more convenient. These alternate procedures are developed in subsequent chapters. Thus we shall show that under appropriate conditions the energy $U(S, V, N_1 \dots)$ may be minimized rather than the entropy $S(U, V, N_1 \dots)$ maximized. That these two procedures determine the same final state is analogous to the fact that a circle may be characterized either as the closed curve of minimum perimeter for a given area or as the closed curve of maximum area for a given perimeter. In later chapters we also introduce several new functions, the minimization of which is logically equivalent to the minimization of the energy or to the maximization of the entropy.

The inversion of the fundamental equation and the alternative statement of the basic extremum principle in terms of a minimum of the energy rather than a maximum of the entropy suggests another viewpoint from which the extremum postulate perhaps may appear plausible. In the theories of electricity and mechanics, ignoring thermal effects, the energy is a function of various mechanical parameters, and the condition of equilibrium is that the energy shall be a minimum. Thus a cone is stable lying on its side, rather than standing on its point, because the first position is of lower energy. If thermal effects are to be included, the energy ceases to be a function simply of the mechanical parameters. According to the inverted fundamental equation, however, the energy is a function of the mechanical parameters and of one additional parameter (the entropy). By the introduction of this additional parameter the form of the energy-minimum principle is extended to the domain of thermal effects as well as to pure mechanical phenomena. In this manner we obtain a sort of correspondence principle between thermodynamics and mechanics—insuring that the thermodynamic equilibrium principle reduces to the mechanical equilibrium principle when thermal effects can be neglected.

We shall see that the mathematical condition that a maximum of $S(U, V, N_1 \dots)$ implies a minimum of $U(S, V, N_1 \dots)$ is that the derivative $(\partial S / \partial U)_{V, N_1 \dots}$ be positive. The motivation for the introduction of this statement in postulate III may be understood in terms of our desire to insure that the entropy maximum principle will go over into an energy minimum principle on inversion of the fundamental equation.

The attention of the reader is called to Appendix B, in which the entropy

is given an atomistic significance in terms of statistical mechanical concepts. Our further considerations do not depend in any way on the material in the Appendix. However, the reader who is plagued by the question "But what is the entropy?" may wish to allay this curiosity by reading Appendix B at this point.

Problems—Section 1.9

1.9-1. The following ten equations are purported to be fundamental equations of various thermodynamic systems. However, five are inconsistent with one or more of postulates II, III, and IV and consequently are not physically acceptable. Find the five that are not physically permissible and indicate the postulate violated by each.

The quantities v_0 , θ , and R are positive constants, and in all cases in which fractional exponents appear only the real positive root is to be taken.

- (a) $S = \left(\frac{R^2}{v_0 \theta}\right)^{1/4} [NVU]^{1/4}$
- (b) $S = \left(\frac{R}{\theta^2}\right)^{1/4} \left[\frac{NU}{V}\right]^{1/4}$
- (c) $S = \left(\frac{R}{\theta}\right)^{1/4} \left[NU - \frac{R\theta V^2}{v_0^2}\right]^{1/4}$
- (d) $S = \left(\frac{R^2 \theta}{v_0^3}\right)^{1/4} V^3 / NU$
- (e) $S = \left(\frac{R^3}{v_0 \theta^2}\right)^{1/4} [N^2 V U^2]^{1/4}$
- (f) $S = NR \ln (UV / N^2 R \theta v_0)$
- (g) $S = \left(\frac{R}{\theta}\right)^{1/4} [NU]^{1/4} \exp(-V^2 / 2N^2 v_0^2)$
- (h) $S = \left(\frac{R}{\theta}\right)^{1/4} [NU]^{1/4} \exp\left(-\frac{UV}{NR \theta v_0}\right)$
- (i) $U = \left(\frac{v_0 \theta}{R}\right) \frac{S^2}{V} \exp(S / NR)$
- (j) $U = \left(\frac{R \theta}{v_0}\right) NV \left(1 + \frac{S}{NR}\right) \exp(-S / NR)$

1.9-2. For each of the five physically acceptable fundamental equations in problem 1.9-1 find U as a function of S , V , and N .

1.9-3. The fundamental equation of system A is

$$S_A = \left(\frac{R^2}{v_0 \theta} \right)^{1/4} [N_A V_A U_A]^{1/4}$$

and that of system B is

$$S_B = \left(\frac{R^2}{v_0 \theta} \right)^{1/4} [N_B V_B U_B]^{1/4}$$

What is the fundamental equation of the composite system $A + B$?

1.9-4. Assume that the internal wall between subsystems A and B in problem 1.9-3 is restrictive with respect to both volume and mole number but non-restrictive with respect to energy; that is, it is rigid, impermeable, and diathermal. Assume that system A has a volume of 9 cm^3 and a mole number of 3 moles. System B has a volume of 4 cm^3 and a mole number of 2 moles. The total energy in the composite system is 20 cal. Plot the entropy against the fraction $U_A/(U_A + U_B)$ of the energy in subsystem A . When the system has come to equilibrium, what are the internal energies of each of the individual subsystems?

The Conditions of Equilibrium

2.1 Intensive Parameters

By virtue of our interest in processes and in the associated changes of the extensive parameters, we anticipate that we shall be concerned with the differential form of the fundamental equation. Writing the fundamental equation in the form

$$U = U(S, V, N_1, N_2, \dots, N_r) \quad (2.1)$$

we compute the first differential:

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V, N_1, \dots, N_r} dS + \left(\frac{\partial U}{\partial V} \right)_{S, N_1, \dots, N_r} dV + \sum_{j=1}^r \left(\frac{\partial U}{\partial N_j} \right)_{S, V, \dots, N_k} dN_j \quad (2.2)$$

The various partial derivatives appearing in the foregoing equation recur so frequently that it is convenient to introduce special symbols for them. They are called *intensive parameters*, and the following notation is conventional:

$$\left(\frac{\partial U}{\partial S} \right)_{V, N_1, \dots, N_r} \equiv T, \quad \text{the temperature} \quad (2.3)$$

$$-\left(\frac{\partial U}{\partial V} \right)_{S, N_1, \dots, N_r} \equiv P, \quad \text{the pressure} \quad (2.4)$$

$$\left(\frac{\partial U}{\partial N_j} \right)_{S, V, \dots, N_k} \equiv \mu_j, \quad \begin{array}{l} \text{the electrochemical potential of} \\ \text{the } j\text{th component} \end{array} \quad (2.5)$$

With this notation, equation 2.2 becomes

$$dU = T dS - P dV + \mu_1 dN_1 + \cdots + \mu_r dN_r \quad (2.6)$$

The formal definition of the temperature soon will be shown to agree with our intuitive qualitative concept, based on the physiological notion of "hot" and "cold." We certainly would be reluctant to adopt a definition of the temperature that would contradict such strongly entrenched although qualitative notions. For the moment, however, we merely introduce the concept of temperature by the formal definition (2.3).

Similarly, we shall soon corroborate that the pressure defined by equation 2.4 agrees in every respect with the pressure defined in mechanics. With respect to the several electrochemical potentials, we have no prior definitions or concepts and we are free to adopt the definition (equation 2.5) forthwith.

For brevity, the electrochemical potential is often referred to simply as the *chemical potential*, and we shall use these two terms interchangeably. However it should be noted that occasionally, and particularly in the theory of solids, the chemical potential is defined as μ minus the molar electrostatic energy.

The term $-P dV$ in equation 2.6 is identified as the quasi-static work dW_M , as given by equation 1.1.

In the special case of constant mole numbers equation 2.6 can then be written as

$$T dS = dU - dW_M \quad \text{if } dN_1 = dN_2 = \cdots = dN_r = 0 \quad (2.7)$$

Recalling our definition of the quasi-static heat, or comparing equation 2.7 with equation 1.2, we now recognize $T dS$ as the quasi-static heat flux.

$$dQ = T dS \quad (2.8)$$

A quasi-static flux of heat into a system is associated with an increase of entropy of that system.

The remaining terms in equation 2.6 represent an increase of internal energy associated with the addition of matter to a system. This type of energy flux, although intuitively meaningful, is not frequently discussed outside thermodynamics and does not have a familiar distinctive name. We shall call $\sum_j \mu_j dN_j$ the *quasi-static chemical work*.

$$dW_c \equiv \sum_{j=1}^r \mu_j dN_j \quad (2.9)$$

Therefore

$$dU = dQ + dW_M + dW_c \quad (2.10)$$

2.2 Equations of State

The temperature, pressure, and the electrochemical potentials are partial derivatives of a function of $S, V, N_1, \cdots, N_r$ and consequently are also functions of $S, V, N_1, \cdots, N_r$. We thus have a set of functional relationships,

$$T = T(S, V, N_1, \cdots, N_r) \quad (2.11)$$

$$P = P(S, V, N_1, \cdots, N_r) \quad (2.12)$$

$$\mu_j = \mu_j(S, V, N_1, \cdots, N_r) \quad (2.13)$$

Such relationships, expressing intensive parameters in terms of the independent extensive parameters, are called *equations of state*.

Knowledge of a single equation of state does *not* constitute complete knowledge of the thermodynamic properties of a system. We shall see, subsequently, that knowledge of *all* the equations of state of a system is equivalent to knowledge of the fundamental equation and consequently is thermodynamically complete.

The fact that the fundamental equation of a system is homogeneous first-order has direct implications for the functional form of the equations of state. It follows immediately that the equations of state are *homogeneous zero-order*. That is, multiplication of each of the independent extensive parameters by a scalar λ leaves the function unchanged.

$$T(\lambda S, \lambda V, \lambda N_1, \cdots, \lambda N_r) = T(S, V, N_1, \cdots, N_r) \quad (2.14)$$

It therefore follows that the temperature of a composite system composed of two identical subsystems is equal to the temperature of either subsystem. This is certainly in agreement with our intuitive concept of temperature. The pressure and the electrochemical potentials also have the property (2.14).

To summarize the foregoing considerations, it is convenient to adopt a condensed notation. We denote the extensive parameters $V, N_1, \cdots, N_r$ by the symbols $X_1, X_2, \cdots, X_t$, so that the fundamental relation takes the form

$$U = U(S, X_1, X_2, \cdots, X_t) \quad (2.15)$$

The intensive parameters are denoted by

$$\left(\frac{\partial U}{\partial S} \right)_{X_1, X_2, \cdots} \equiv T = T(S, X_1, X_2, \cdots, X_t) \quad (2.16)$$

$$\left(\frac{\partial U}{\partial X_j} \right)_{S, \cdots, X_t} \equiv P_j = P_j(S, X_1, X_2, \cdots, X_t) \quad j = 1, 2, \cdots, t \quad (2.17)$$

whence

$$dU = T dS + \sum_{j=1}^t P_j dX_j \quad (2.18)$$

is, in one case the entropy is a member of the set of independent parameters, and in the second case the energy is such a member. In performing formal manipulations in thermodynamics, it is extremely important to make a definite commitment to one or the other of these choices and to adhere rigorously to that choice. A great deal of confusion results from a vacillation between these two alternatives within a single problem.

If the entropy is considered dependent and the energy, independent, as in $S = S(U \cdots X_k \cdots)$, we shall refer to the analysis as being in the *entropy representation*. If the energy is dependent and the entropy is independent, as in $U = U(S \cdots X_k \cdots)$, we shall refer to the analysis as being in the *energy representation*.

The formal development of thermodynamics can be carried out in either the energy or entropy representations alone, but for the solution of a particular problem either one or the other representation may prove to be by far the more convenient. Accordingly, we shall develop the two representations in parallel, although a discussion presented in one representation generally requires only a brief outline in the alternate representation.

The relation $S = S(X_0 \cdots X_j \cdots)$ is said to be the *entropic fundamental relation*, the set of variables $X_0 \cdots X_j \cdots$ is called the *entropic extensive parameters*, and the set of variables $F_0 \cdots F_j \cdots$ is called the *entropic intensive parameters*. Similarly, the relation $U = U(S, X_1 \cdots X_j \cdots)$ is said to be the *energetic fundamental relation*, the set of variables $S, X_1 \cdots X_j \cdots$ is called the *energetic extensive parameters*, and the set of variables $P_1 \cdots P_j \cdots$ is called the *energetic intensive parameters*.

Problems—Section 2.3

2.3-1. Find the three equations of state in the entropy representation for a system with the fundamental equation

$$u = \left(\frac{v_0^{1/2} \theta}{R^{1/2}} \right) \frac{s^{3/2}}{v^{1/2}}$$

2.3-2. Show by a diagram (drawn to arbitrary scale) the dependence of temperature on volume for fixed pressure for the system of problem 2.3-1. Draw two such "isobars," corresponding to two values of the pressure, and indicate which isobar corresponds to the higher pressure.

2.3-3. Find the three equations of state in the entropy representation for a system with the fundamental equation

$$u = \left(\frac{\theta}{R} \right) s^2 e^{v^2/v_0^2}$$

2.4 Thermal Equilibrium—Temperature

We are now in a position to illustrate several interesting implications of the extremum principle which we have postulated for the entropy. Consider a closed composite system consisting of two simple systems separated by a wall that is rigid and impermeable to matter but that does allow the flow of heat. The volumes and mole numbers of each of the simple systems are fixed, but the energies $U^{(1)}$ and $U^{(2)}$ are free to change, subject to the conservation restriction

$$U^{(1)} + U^{(2)} = \text{constant} \quad (2.30)$$

imposed by the closure of the composite system as a whole. Assuming that the system has come to equilibrium, we wish to find the values of $U^{(1)}$ and $U^{(2)}$. Now, by our fundamental postulate, the values of $U^{(1)}$ and $U^{(2)}$ are such as to maximize the entropy. Therefore, by the usual mathematical condition for an extremum, we conclude that in the equilibrium state a virtual infinitesimal transfer of energy from system 1 to system 2 will produce no change in the entropy of the whole system. That is,

$$dS = 0 \quad (2.31)$$

The additivity of the entropy for the two subsystems gives the relation

$$S = S^{(1)}(U^{(1)}, V^{(1)} \cdots N_j^{(1)} \cdots) + S^{(2)}(U^{(2)}, V^{(2)} \cdots N_j^{(2)} \cdots). \quad (2.32)$$

As $U^{(1)}$ and $U^{(2)}$ are changed by the virtual energy transfer, the entropy change is

$$dS = \left(\frac{\partial S^{(1)}}{\partial U^{(1)}} \right)_{V^{(1)} \cdots N_j^{(1)} \cdots} dU^{(1)} + \left(\frac{\partial S^{(2)}}{\partial U^{(2)}} \right)_{V^{(2)} \cdots N_j^{(2)} \cdots} dU^{(2)} \quad (2.33)$$

or, employing our definition of the temperature,

$$dS = \frac{1}{T^{(1)}} dU^{(1)} + \frac{1}{T^{(2)}} dU^{(2)} \quad (2.34)$$

By the conservation condition (equation 2.30), we have

$$dU^{(2)} = -dU^{(1)} \quad (2.35)$$

whence

$$dS = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) dU^{(1)} \quad (2.36)$$

The condition of equilibrium (equation 2.31) demands that dS vanish for arbitrary values of $dU^{(1)}$, whence

$$\frac{1}{T^{(1)}} = \frac{1}{T^{(2)}} \quad (2.37)$$

This is the condition of equilibrium. If the fundamental equations of each of the subsystems were known, then $1/T^{(1)}$ would be a known function of $U^{(1)}$ (and also of $V^{(1)}$ and $N_k^{(1)}$... , which, however, are merely constants). Similarly, $1/T^{(2)}$ would be a known function of $U^{(2)}$, and the equation $1/T^{(1)} = 1/T^{(2)}$ would be one equation in $U^{(1)}$ and $U^{(2)}$. The conservation condition $U^{(1)} + U^{(2)} = \text{constant}$ provides a second equation, and these two equations completely determine, in principle, the values of $U^{(1)}$ and of $U^{(2)}$. To proceed further and actually to obtain the values of $U^{(1)}$ and of $U^{(2)}$ would require knowledge of the explicit forms of the fundamental equations of the systems. In thermodynamic theory, however, we accept the existence of the fundamental equations, but we do not assume explicit forms for them, and we therefore do not obtain explicit answers. In practical applications of thermodynamics the fundamental equations may be known, either by empirical observations (in terms of measurements to be described later) or on the basis of statistical mechanical calculations based on simple models. In this way applied thermodynamics is able to lead to explicit numerical answers.

Equation 2.37 could also be written as $T^{(1)} = T^{(2)}$. We write it in the form $1/T^{(1)} = 1/T^{(2)}$ to stress the fact that our analysis is couched in the entropy representation. By writing $1/T^{(1)}$, we indicate a function of $U^{(1)}$, $V^{(1)}$... , whereas $T^{(1)}$ would imply a function of $S^{(1)}$, $V^{(1)}$ The physical significance of equation 2.37, however, remains the equality of the temperatures of the two subsystems.

A second phase of the problem is the investigation of the stability of the predicted final state. In the solution given we have not exploited fully the basic postulate that the entropy is a maximum in equilibrium, but we merely have investigated the consequences of the fact that it is an extremum. The condition that it be a maximum requires, in addition to the condition $dS = 0$, that

$$d^2S < 0 \quad (2.38)$$

The consequences of this condition lead to considerations of stability, to which we shall give explicit attention in Chapter 8.

2.5 Agreement with Intuitive Concept of Temperature

In the foregoing example we have seen that if two systems are separated by a diathermal wall heat will flow until each of the systems attains the same temperature. This prediction is in agreement with our intuitive notion of temperature, and it is the first of several observations that corroborate the plausibility of our formal definition of the temperature.

Inquiring into our example in slightly more detail, we suppose that

the two subsystems are initially separated by an adiabatic wall and that the temperatures of the two subsystems are almost, but not quite, equal. In particular let us assume that

$$T^{(1)} > T^{(2)} \quad (2.39)$$

The system is considered to be in equilibrium with respect to the internal adiabatic constraint. If, now, the internal adiabatic constraint is removed, the system is no longer in equilibrium, heat flows across the wall, and the entropy of the composite system *increases*. Finally the system comes to a new equilibrium state, determined by the condition that the final values of $T^{(1)}$ and $T^{(2)}$ are equal and with the maximum possible value of the entropy that is consistent with the remaining constraints. Let us now compare the initial and the final states. If ΔS denotes the entropy difference between the final and initial states, we have

$$\Delta S > 0 \quad (2.40)$$

But, as in equation 2.34, we find

$$\Delta S \simeq \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) \Delta U^{(1)} \quad (2.41)$$

where $T^{(1)}$ and $T^{(2)}$ are the initial values of the temperatures. By the condition that $T^{(1)} > T^{(2)}$, we now find that

$$\Delta U^{(1)} < 0 \quad (2.42)$$

This means that the spontaneous process that occurred was one in which heat flowed *from* subsystem 1 *to* subsystem 2. We conclude therefore that heat tends to flow *from* a system with a *high* value of T *to* a system with a *low* value of T . This is again in agreement with our intuitive notion of the temperature. It should be noted that these conclusions do not depend on our assumption that $T^{(1)}$ is approximately equal to $T^{(2)}$; this assumption was made merely for the purpose of obtaining mathematical simplicity in equation 2.41, which otherwise would require a formulation in terms of integrals.

If we now take stock of our intuitive notion of temperature, based on the physiological sensations of hot and cold, we realize that it is based upon two essential properties. First, we expect temperature to be an intensive parameter, having the same value in a part of a system as it has in the entire system. Second, we expect that heat should tend to flow from regions of high temperature toward regions of low temperature. These properties imply that thermal equilibrium is associated with equality and homogeneity of the temperature. We have demonstrated that our

formal definition of the temperature possesses each of these properties, so that we have now corroborated that our definition is intuitively satisfactory.

2.6 Temperature Units

The physical dimensions of temperature are those of energy divided by those of entropy. But we have not yet committed ourselves on the dimensions of entropy; in fact its dimensions can be selected quite arbitrarily. For if the entropy is multiplied by any dimensional constant, we obtain a new function of different dimensions but with exactly the same extremum properties and therefore also quite acceptable as the entropy. The only restriction we must maintain is that the product of temperature and entropy have the dimensions of energy. We summarily resolve the arbitrariness simply by adopting the convention that the entropy is dimensionless; from the more incisive viewpoint of statistical mechanics, this is a physically reasonable choice. Consequently the dimensions of temperature are identical to those of energy. However, just as torque and work have the same dimensions, but are very different types of quantities and are measured in different units (the cm-dyne and the erg, respectively), so the temperature and the energy must be carefully distinguished. The *dimensions* of both energy and temperature are $[\text{mass} \cdot (\text{length})^2/(\text{time})^2]$. The *units* of energy are joules, ergs, calories, etc. The units of temperature remain to be discussed.

In our later discussion of thermodynamic engines and of the Carnot cycle we show that the ratio of the temperatures of two given systems can be measured directly and unambiguously. The measurability of the ratio of temperatures determines the scale of temperature, except for an arbitrary multiplicative constant. The temperature of some arbitrarily chosen standard system may be assigned at will, and the temperatures of all other systems are then uniquely determined, with values directly proportional to the chosen temperature of the fiducial system.

Various choices of a fiducial system, and various assignments of its temperature, lead to different scales of temperature. The *absolute Kelvin* scale of temperature is obtained by assigning the number 273.16 to the temperature of a mixture of pure ice, water, and water vapor in mutual equilibrium; a state which we show in our later discussion of "triple points" to determine a unique temperature. The corresponding unit of temperature is called a *degree Kelvin*, designated by the notation $^{\circ}\text{K}$. The temperature of the ice-water vapor system then is 273.16°K .

The *absolute Fahrenheit* scale is obtained by assigning the temperature $9/5(273.16) = 491.688^{\circ}\text{R}$ to the ice-water-vapor system referred to. The

unit, denoted by $^{\circ}\text{R}$, is called the *absolute Fahrenheit degree*, or the *degree Rankine*. Absolute Fahrenheit temperatures are merely $5/9$ times the corresponding absolute Kelvin temperature.

The definitions cited are those adopted by the Tenth General Conference of Weights and Measures in 1954, and by universal acceptance they supplant the earlier definitions in terms of two fixed points.

Closely related to the absolute Kelvin scale of temperature is the *international Kelvin* scale, which is a "practical" scale, defined in terms of the properties of particular systems in various temperature ranges and contrived to coincide as closely as possible with the absolute Kelvin scale. The practical advantage of the international Kelvin scale is that it provides reproducible laboratory standards for temperature measurement throughout the temperature range. However, from the thermodynamic point of view it is not a true temperature scale at all, and to the extent that it deviates from the absolute scale it will not yield temperature ratios that are consistent with those demanded by the thermodynamic formalism.

Still another scale of temperature is the *thermodynamic Celsius* scale. The unit of temperature is the *degree Celsius*, denoted by $^{\circ}\text{C}$, and this unit is identical in size with the absolute degree Kelvin. The thermodynamic Celsius temperatures are defined (by the 1954 agreement) as 273.15 less than Kelvin temperatures. The temperature of ice, water, and water-vapor in equilibrium is 0.01°C . However, the temperature of a mixture of ice and water at 1 atm pressure is very nearly 0°C , with the error appearing only in the third decimal place, and the temperature of boiling water at 1 atm pressure is approximately 100°C . Consequently, the Celsius scale provides convenient numbers for general use.

Clearly the Celsius scale yields different temperature ratios than the Kelvin scale, and consequently the Celsius scale is *not* an acceptable scale for thermodynamic use. Celsius temperatures must be converted into Kelvin temperatures (merely by the addition of 273.15) before substitution in thermodynamic formulas.

Prior to the 1954 international agreement, the Celsius scale was referred to in many countries, including the United States, as the *Centigrade scale*.

An international Celsius scale is defined as bearing the same relationship to the international Kelvin scale as the thermodynamic Celsius scale bears to the absolute Kelvin scale. To the accuracy that will generally concern us, we need make no distinction between the two Kelvin scales nor between the two Celsius scales, but the difference in principle should be kept in mind.

Finally, a Fahrenheit scale is defined in terms of the absolute Fahrenheit scale by subtraction of 459.67. This number is exactly $9/5(273.15) - 32$.

It follows that conversion of a Celsius temperature to a Fahrenheit temperature involves multiplication by $\frac{9}{5}$ and addition of 32. The temperature of ice and water at 1 atm pressure is about 32°F, the temperature of boiling water at 1 atm pressure is about 212°F, and room temperatures are in the vicinity of 70°F.

Although we have defined the temperature formally in terms of a partial derivative of the fundamental relation, we note briefly, in conclusion, the conventional method of introduction of the temperature concept, as developed by Kelvin and Caratheodory. The heat flux dQ is first defined very much as we have introduced it in connection with the energy conservation principle. From the consideration of certain cyclic processes it is then inferred that there exists an integrating factor ($1/T$) such that the product of this integrating factor with the imperfect differential dQ is a perfect differential (dS).

$$dS = \frac{1}{T} dQ \quad (2.43)$$

The temperature and the entropy thereby are introduced by analysis of the existence of integrating factors in particular types of differential equations called *Pfaffian forms*.

Problems—Section 2.6

2.6-1. The temperature of a system composed of ice, water, and water-vapor in mutual equilibrium has a temperature of *exactly* 273.16°K, by definition. The temperature of a system of ice and water at 1 atm of pressure is then measured as 273.15°K, with the third and later decimal places uncertain. The temperature of a system of water and water-vapor (i.e. boiling water) at 1 atm is measured as 373.15°K $\pm$ 0.01°K. Compute the temperature of water–water-vapor at 1 atm, with its probable error, on the Celsius, absolute Fahrenheit, and Fahrenheit scales.

2.6-2. The "gas constant" R is a constant having the value $R = 1.986$ cal/mole°K. Since the size of the Celsius degree is the same as the Kelvin degree, it also has the value 1.986 cal/mole°C. Express R in units of joules/mole°F.

2.6-3. Two particular systems have the following equations of state:

$$\frac{1}{T^{(1)}} = \frac{3}{2} R \frac{N^{(1)}}{U^{(1)}}$$

and

$$\frac{1}{T^{(2)}} = \frac{5}{2} R \frac{N^{(2)}}{U^{(2)}}$$

where R is a constant having the value 1.986 cal/mole°K. The mole number of the first system is $N^{(1)} = 2$, and that of the second is $N^{(2)} = 3$. The two systems

are separated by a diathermal wall, and the total energy in the composite system is 6000 cal. What is the internal energy of each system in equilibrium?

2.6-4. Two systems with the equations of state given in problem 2.6-3 are separated by a diathermal wall. The respective mole numbers are $N^{(1)} = 2$ and $N^{(2)} = 3$. The initial temperatures are $T^{(1)} = 250^\circ\text{K}$ and $T^{(2)} = 350^\circ\text{K}$. What are the values of $U^{(1)}$ and $U^{(2)}$ after equilibrium has been established? What is the equilibrium temperature?

2.7 Mechanical Equilibrium

A second application of the extremum principle for the entropy yields an even simpler result and therefore is useful in making the procedure clear. We consider a closed composite system consisting of two simple systems separated by a movable diathermal wall that is impervious to the flow of matter. The values of the mole numbers are fixed and constant, but the values of $U^{(1)}$ and $U^{(2)}$ may change, subject only to the closure condition

$$U^{(1)} + U^{(2)} = \text{constant} \quad (2.44)$$

and the values of $V^{(1)}$ and $V^{(2)}$ may change, subject only to the closure condition

$$V^{(1)} + V^{(2)} = \text{constant} \quad (2.45)$$

The extremum principle requires that no change in entropy result from infinitesimal virtual processes consisting of transfer of heat across the wall and displacement of the wall.

Then

$$dS = 0 \quad (2.46)$$

where

$$dS = \left(\frac{\partial S^{(1)}}{\partial U^{(1)}} \right)_{V^{(1)} \dots N_k^{(1)} \dots} dU^{(1)} + \left(\frac{\partial S^{(1)}}{\partial V^{(1)}} \right)_{U^{(1)} \dots N_k^{(1)} \dots} dV^{(1)} \\ + \left(\frac{\partial S^{(2)}}{\partial U^{(2)}} \right)_{V^{(2)} \dots N_k^{(2)} \dots} dU^{(2)} + \left(\frac{\partial S^{(2)}}{\partial V^{(2)}} \right)_{U^{(2)} \dots N_k^{(2)} \dots} dV^{(2)} \quad (2.47)$$

By the closure conditions

$$dU^{(2)} = -dU^{(1)} \quad (2.48)$$

and

$$dV^{(2)} = -dV^{(1)} \quad (2.49)$$

whence

$$dS = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) dU^{(1)} + \left(\frac{P^{(1)}}{T^{(1)}} - \frac{P^{(2)}}{T^{(2)}} \right) dV^{(1)} = 0 \quad (2.50)$$

As this expression must vanish for arbitrary and independent values of $dU^{(1)}$ and $dV^{(1)}$, we must have

$$\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} = 0 \quad (2.51)$$

and

$$\frac{P^{(1)}}{T^{(1)}} - \frac{P^{(2)}}{T^{(2)}} = 0 \quad (2.52)$$

Although these two equations are the equilibrium conditions in the proper form, appropriate to the entropy representation, we note that they imply the physical conditions of equality of both temperature and pressure.

$$T^{(1)} = T^{(2)} \quad (2.53)$$

$$P^{(1)} = P^{(2)} \quad (2.54)$$

The equality of the temperatures is just our previous result for equilibrium with a diathermal wall. The equality of the pressures is the new feature introduced by the fact that the wall is movable. Of course, the equality of the pressures is precisely the result that we would expect on the basis of mechanics, and this result corroborates our identification of the function P as the mechanical pressure.

The reader may ask why we have considered the problem of a movable diathermal wall rather than the ostensibly simpler case of a movable adiabatic wall. The latter, unfortunately, is a subtle problem lacking a unique physical answer. As the difficulties of this problem are quite specialized, we shall not consider it here, but a discussion is given in Appendix C for the interested reader.

Problems—Section 2.7

2.7-1. Two particular systems have the following equations of state:

$$\frac{1}{T^{(1)}} = \frac{3}{2} R \frac{N^{(1)}}{U^{(1)}}, \quad \frac{P^{(1)}}{T^{(1)}} = R \frac{N^{(1)}}{V^{(1)}}$$

and

$$\frac{1}{T^{(2)}} = \frac{5}{2} R \frac{N^{(2)}}{U^{(2)}}, \quad \frac{P^{(2)}}{T^{(2)}} = R \frac{N^{(2)}}{V^{(2)}}$$

where $R = 1.986 \text{ cal/mole}^\circ\text{K}$. The mole number of the first system is $N^{(1)} = 0.5$, and that of the second is $N^{(2)} = 0.75$. The two systems are contained in a closed cylinder, separated by a movable diathermal piston. The initial temperatures are $T^{(1)} = 200^\circ\text{K}$ and $T^{(2)} = 300^\circ\text{K}$, and the total volume is 20 liters. What is the energy and the volume of each system in equilibrium? What is the pressure and the temperature?

2.8 Equilibrium with Respect to Matter Flow

A final example employing the entropy maximum principle gives some insight into the nature of the chemical potential. We consider the equilibrium state of two simple systems connected by a rigid and diathermal wall, permeable to one type of material (N_1) and impermeable to all others ($N_2, N_3, \dots, N_r$). We thus seek the equilibrium values of $U^{(1)}$ and $U^{(2)}$ and of $N_1^{(1)}$ and $N_1^{(2)}$. The virtual change in entropy in the appropriate virtual process is

$$dS = \frac{1}{T^{(1)}} dU^{(1)} - \frac{\mu_1^{(1)}}{T^{(1)}} dN_1^{(1)} + \frac{1}{T^{(2)}} dU^{(2)} - \frac{\mu_1^{(2)}}{T^{(2)}} dN_1^{(2)} \quad (2.55)$$

and the closure conditions demand

$$dU^{(2)} = -dU^{(1)} \quad (2.56)$$

and

$$dN_1^{(2)} = -dN_1^{(1)} \quad (2.57)$$

whence

$$dS = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) dU^{(1)} - \left(\frac{\mu_1^{(1)}}{T^{(1)}} - \frac{\mu_1^{(2)}}{T^{(2)}} \right) dN_1^{(1)} \quad (2.58)$$

As dS must vanish for arbitrary values of both $dU^{(1)}$ and $dN_1^{(1)}$, we find as the conditions of equilibrium

$$\frac{1}{T^{(1)}} = \frac{1}{T^{(2)}} \quad (2.59)$$

and

$$\frac{\mu_1^{(1)}}{T^{(1)}} = \frac{\mu_1^{(2)}}{T^{(2)}} \quad (\text{whence also } \mu_1^{(1)} = \mu_1^{(2)}) \quad (2.60)$$

Thus, just as the temperature can be looked upon as a sort of "potential" for heat flux and the pressure can be looked upon as a sort of "potential" for volume changes, so the chemical potential can be looked upon as a sort of "potential" for matter flux. A difference in chemical potential provides a "generalized force" for matter flow.

The direction of the matter flow can be analyzed by the same method used in section 2.5 to analyze the direction of the heat flow. If we assume that the temperatures $T^{(1)}$ and $T^{(2)}$ are equal, equation 2.58 becomes

$$dS = \frac{\mu_1^{(2)} - \mu_1^{(1)}}{T} dN_1^{(1)} \quad (2.61)$$

If $\mu_1^{(1)}$ is greater than $\mu_1^{(2)}$, $dN_1^{(1)}$ will be negative, since dS must be

positive. Thus matter tends to flow from regions of high chemical potential to regions of low chemical potential.

In later chapters we shall see that the chemical potential provides the generalized force not only for the flow of matter from point to point but also for its changes of phase and for chemical reactions. The chemical potential thus plays a dominant role in theoretical chemistry.

The units of electrochemical potential are calories per mole, joules per mole, or any desired energy unit per mole.

Problems—Section 2.8

2.8-1. The fundamental equation of a particular type of two-component system is

$$S = NA + NR \ln \frac{U^{3/4} V}{N^{3/4}} - N_1 R \ln \frac{N_1}{N} - N_2 R \ln \frac{N_2}{N}$$

$$N \equiv N_1 + N_2$$

where $R = 1.986 \text{ cal/mole}^\circ\text{K}$ and where A is an unspecified constant. A closed rigid cylinder of total volume 10 liters is divided into two chambers of equal volume by a diathermal rigid membrane, permeable to the first component but impermeable to the second. In one chamber is placed a sample of the system with original parameters $N_1^{(1)} = 0.5$, $N_2^{(1)} = 0.75$, $V^{(1)} = 5$ liters, and $T^{(1)} = 300^\circ\text{K}$. In the second chamber is placed a sample with original parameters $N_1^{(2)} = 1$, $N_2^{(2)} = 0.5$, $V^{(2)} = 5$ liters, and $T^{(2)} = 250^\circ\text{K}$. After equilibrium is established, what are the values of $N_1^{(1)}$, $N_1^{(2)}$, T , $P^{(1)}$ and $P^{(2)}$?

Some Formal Relationships

3.1 The Euler Equation

Having seen how the fundamental postulates lead to a solution of the equilibrium problem, we now pause to examine in somewhat greater detail the mathematical properties of fundamental equations.

The homogeneous first-order property of the fundamental relation permits that equation to be written in a particularly convenient form, called the Euler form.

From the definition of the homogeneous first-order property we have, for any λ ,

$$U(\lambda S, \lambda X_1 \cdots \lambda X_t) = \lambda U(S, X_1 \cdots X_t) \quad (3.1)$$

Differentiating with respect to λ ,

$$\frac{\partial U(\cdots \lambda X_k \cdots)}{\partial(\lambda S)} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U(\cdots \lambda X_k \cdots)}{\partial(\lambda X_j)} \frac{\partial(\lambda X_j)}{\partial \lambda} + \cdots = U(S, X_1 \cdots X_t) \quad (3.2)$$

or

$$\frac{\partial U(\cdots \lambda X_k \cdots)}{\partial(\lambda S)} S + \cdots \frac{\partial U(\cdots \lambda X_k)}{\partial(\lambda X_j)} X_j + \cdots = U(S, X_1 \cdots X_t) \quad (3.3)$$

This equation is true for any λ and in particular for $\lambda = 1$, in which case it takes the form

$$\frac{\partial U}{\partial S} S + \cdots \frac{\partial U}{\partial X_j} X_j + \cdots = U \quad (3.4)$$

$$U = TS + \sum_{j=1}^t P_j X_j \quad (3.5)$$

For a simple system in particular we have

$$U = TS - PV + \mu_1 N_1 + \cdots + \mu_r N_r \quad (3.6)$$

The relation 3.5 or 3.6 is the particularization to thermodynamics of the Euler theorem on homogeneous first-order forms. The foregoing development merely reproduces the standard mathematical derivation. We refer to equation 3.5 or 3.6 as the Euler relation.

In the entropy representation the Euler relation takes the form

$$S = \sum_{j=0}^t F_j X_j \quad (3.7)$$

or

$$S = \left(\frac{1}{T}\right)U + \left(\frac{P}{T}\right)V - \sum_{k=1}^r \left(\frac{\mu_k}{T}\right)N_k \quad (3.8)$$

Problems—Section 3.1

3.1-1. Write each of the five physically acceptable fundamental equations of problem 1.9-1 in the Euler form.

3.2 The Gibbs-Duhem Relation

In Chapter 2 we arrived at equilibrium criteria involving the temperature, pressure, and the chemical potentials. Each of the intensive parameters entered the theory in a similar way, and the formalism is, in fact, symmetric in the several intensive parameters. In spite of this symmetry, however, the reader is apt to feel that he has an intuitive response to the concepts of temperatures and pressure, which is lacking, at least to some degree, in the case of the chemical potential. It is of some interest, then, to note that the intensive parameters are not all independent. There is a relation among the intensive parameters, and for a single-component system μ is a function of T and P .

The existence of a relationship among the various intensive parameters is a consequence of the homogeneous first-order property of the fundamental relation. For a single component system this property permits the fundamental relation to be written in the form $u = u(s, v)$, as in equation 2.19. Each of the three intensive parameters is then also a function of s and v . Elimination of s and v from among the three equations of state yields a relation among T , P , and μ .

The argument can easily be extended to the more general case and again consists of a straightforward counting of variables. Suppose we have a fundamental equation in $(t+1)$ extensive variables

$$U = U(S, X_1, X_2, \cdots, X_t) \quad (3.9)$$

yielding, in turn, $t+1$ equations of state

$$P_k = P_k(S, X_1, X_2, \cdots, X_t) \quad (3.10)$$

If we choose the parameter λ of equation 2.14 as $\lambda = 1/X_t$, we then have

$$P_k = P_k(S/X_t, X_1/X_t, \cdots, X_{t-1}/X_t, 1) \quad (3.11)$$

Thus each of the $(t+1)$ intensive parameters is a function of just t variables. Elimination of these t variables among the $(t+1)$ equations yields the desired relation among the intensive parameters.

To find the explicit functional relationship that exists among the set of intensive parameters would require knowledge of the explicit fundamental equation of the system. That is, the analytic form of the relationship varies from system to system. Given the fundamental relation, the procedure is evident and follows the sequence of steps indicated by equations 3.9-3.11.

A differential form of the relation among the intensive parameters can be obtained directly from the Euler relation and is known as the Gibbs-Duhem relation. Taking the infinitesimal variation of equation 3.5, we find

$$dU = T dS + S dT + \sum_{j=1}^t P_j dX_j + \sum_{j=1}^t X_j dP_j \quad (3.12)$$

But, in accordance with equation 2.6, we certainly know that

$$dU = T dS + \sum_{j=1}^t P_j dX_j \quad (3.13)$$

whence, by subtraction we find the Gibbs-Duhem relation

$$S dT + \sum_{j=1}^t X_j dP_j = 0 \quad (3.14)$$

For a single-component simple system, in particular, we have

$$S dT - V dP + N d\mu = 0 \quad (3.15)$$

or

$$d\mu = -s dT + v dP \quad (3.16)$$

The variation in chemical potential is not independent of the variations of temperature and pressure, but the variation of any one can be computed in terms of the variations of the other two.

The Gibbs-Duhem relation presents the relationship among the intensive parameters in differential form. Integration of this equation yields the relation in explicit form, and this is a procedure alternative to

that presented in equations 3.9–3.11. In order to integrate the Gibbs–Duhem relation, one must know the equations of state which enable one to write the X_j 's in terms of the P_j 's, or vice versa.

The number of intensive parameters capable of independent variation is called the number of *thermodynamic degrees of freedom* of a given system. A simple system of r components has $r + 1$ thermodynamic degrees of freedom.

In the entropy representation the Gibbs–Duhem relation again states that the sum of products of the extensive parameters and the differentials of the corresponding intensive parameters vanishes.

$$\sum_{j=0}^t X_j dF_j = 0 \quad (3.17)$$

or

$$Ud\left(\frac{1}{T}\right) + Vd\left(\frac{P}{T}\right) - \sum_{k=1}^r N_k d\left(\frac{\mu_k}{T}\right) = 0 \quad (3.18)$$

Problems—Section 3.2

3.2–1. Find the relation among T , P , and μ for the system with the fundamental equation

$$U = \left(\frac{v_0 \theta}{R^2}\right) \frac{S^3}{NV}$$

3.3 Summary of Formal Structure

Let us now summarize the structure of the thermodynamic formalism in the energy representation. For the sake of clarity, and in order to be explicit, we consider a single-component simple system. The fundamental equation

$$U = U(S, V, N) \quad (3.19)$$

contains *all* thermodynamic information about a system. With the definitions $T = \partial U / \partial S$, etc., the fundamental equation implies three equations of state:

$$T = T(S, V, N) = T(s, v) \quad (3.20)$$

$$P = P(S, V, N) = P(s, v) \quad (3.21)$$

$$\mu = \mu(S, V, N) = \mu(s, v) \quad (3.22)$$

If all three equations of state are known, they may be substituted into the Euler relation, thereby recovering the fundamental equation. Thus the totality of all three equations of state is equivalent to the fundamental

equation and contains all thermodynamic information about a system. Any single equation of state contains less thermodynamic information than the fundamental equation.

If two equations of state are known, the Gibbs–Duhem relation may be integrated to obtain the third. The equation of state so obtained will contain an undetermined integration constant. Thus two equations of state suffice to determine the fundamental equation, except for an undetermined constant.

An alternative procedure for obtaining the fundamental equation when only two equations of state are given is by direct integration of the molar relation

$$du = T ds - P dv \quad (3.23)$$

Clearly, knowledge of $T = T(s, v)$ and $P = P(s, v)$ yields a differential equation in the three variables u , s , and v , and integration gives

$$u = u(s, v) \quad (3.24)$$

which is a fundamental equation. Again, of course, we have an undetermined constant of integration.

It is always possible to express the internal energy as a function of parameters other than S , V , and N . Thus we could eliminate S from $U = U(S, V, N)$ and $T = T(S, V, N)$ to obtain an equation of the form $U = U(T, V, N)$. However, we wish to stress that such an equation is *not* a fundamental relation and does not contain all possible thermodynamic information about the system. In fact, recalling the definition of T as $\partial U / \partial S$, we see that $U = U(T, V, N)$ actually is a partial differential equation. Even if this equation were integrable, it would yield a fundamental equation with undetermined functions. Thus knowledge of the relation $U = U(S, V, N)$ allows one to compute the relation $U = U(T, V, N)$, but knowledge of $U = U(T, V, N)$ does not permit one inversely to compute $U = U(S, V, N)$. Associated with every equation there is both a truth-value and an informational content. Each of the equations $U = U(S, V, N)$ and $U = U(T, V, N)$ may be true, but only the former has the optimum informational content.

3.4 An Example—The Ideal Monatomic Gas

An ideal monatomic gas is characterized by the two equations

$$PV = NRT \quad (3.25)$$

and

$$U = \frac{3}{2} NRT \quad (3.26)$$

in which R is a constant with the value 1.986 cal/mole °K.

Now let ϕ be a function of the form

$$\phi \equiv (\delta \hat{X}_0)^{n_0} (\delta \hat{X}_1)^{n_1} \cdots (\delta \hat{X}_s)^{n_s} \quad (d)$$

in which the n_j are nonnegative integers. Using the result proved above, show that

$$\langle \phi \delta \hat{F}_k \rangle = -k \left\langle \frac{\partial \phi}{\partial \delta \hat{X}_k} \right\rangle = -k n_k \langle \phi / \delta \hat{X}_k \rangle \quad (e)$$

Consider now the quantity $\langle \phi \delta \hat{X}_k \rangle$ and, using equations (b) and (e), show that

$$\langle \phi \delta \hat{X}_k \rangle = -k \sum_j S_{jk} n_j \langle \phi / \delta \hat{X}_j \rangle \quad (f)$$

Finally, show that if $\phi = 1$ we obtain $\langle \delta \hat{X}_k \rangle = 0$, that if $\phi = \delta \hat{X}_j$ we obtain equation 15.47, and that other choices of ϕ permit calculation of higher moments.

Irreversible Thermodynamics

16.1 General Remarks

As useful as the characterization of equilibrium states by thermostatic theory has proved to be, it must be conceded that our primary interest is frequently in processes rather than in states. In biology, particularly, it is the life process that captures our imagination rather than the eventual equilibrium state to which each organism inevitably proceeds. Thermostatics does provide two methods that permit us to infer some limited information about processes, but each of these methods is indirect and each yields only the most meager return. First, by studying the initial and terminal equilibrium states, it is sometimes possible to bracket a process and thence to determine the effect of the process in its totality. Second, if some process occurs *extremely* slowly, we may compare it with an idealized, nonphysical, quasi-static process. But neither of these methods confronts the central problem of *rates* of real physical processes.

The extension of thermodynamics which has reference to the rates of physical processes is the theory of *irreversible thermodynamics*.

Two basic postulates underlie equilibrium statistical mechanics. The first postulate concerns the existence of an enormous number of atomistic states among which continual spontaneous transitions occur in the course of a macroscopic observation. The second is the assumption of equal a priori probability of each of the atomistic states. From these extremely general hypotheses follows the entire general theory of statistical mechanics, culminating in the theorems that, in turn, constitute the postulates of thermostatics. Because of the general nature of the postulates, the predictions of thermostatics are similarly general. The numerical values

of specific heats, compressibilities, and the like are not predicted, but certain general relationships among these quantities are predicted.

The theory of nonequilibrium statistical mechanics is based on the two postulates of the equilibrium theory, plus the additional postulate of *time symmetry of physical laws*. This additional postulate states that *all the laws of physics remain unchanged if the time t is everywhere replaced by its negative $-t$ and if simultaneously the magnetic field $\mathbf{H}_e$ is replaced by its negative $-\mathbf{H}_e$* .

From the general postulates of nonequilibrium statistical mechanics there follows an extensive theory, culminating in several theorems that, in turn, constitute the postulates of irreversible thermodynamics. From these we derive thermodynamic theorems of a general nature, expressing relationships among various dynamical quantities.

The first such result was the Onsager reciprocity theorem, which expresses a certain symmetry in the response of two simultaneously occurring processes. Another theorem is the fluctuation-dissipation theorem of H. Callen and T. Welton, which expresses a relation between irreversible response and equilibrium fluctuations. Other theorems relating to the fluctuations during an irreversible process, and involving extensions to nonlinear processes, have been developed by W. Bernard and H. Callen and by M. Lax.

Despite the considerable number of results of nonequilibrium thermodynamics, by far the most practically significant result is the Onsager reciprocity theorem. Consequently, we restrict our attention to this theorem alone. We indicate in section 16.5 how this theorem is related to the underlying postulate of time symmetry.

16.2 Affinities and Fluxes

Preparatory to our discussion of the Onsager theorem, we define certain quantities that appropriately describe irreversible processes. Basically we require two types of parameters: one to describe the "force" that drives a process and one to describe the response to this force.

The processes of most general interest occur in continuous systems, such as the flow of energy in a bar with a continuous temperature gradient. However, to suggest the proper way to choose parameters in such continuous systems, we first consider the relatively simple case of a discrete system. A typical process in a discrete system would be the flow of energy from one homogeneous subsystem to another through an infinitely thin diathermal partition.

Consider a composite system composed of two subsystems. An extensive parameter has values X_k and X'_k in the two subsystems, and

the closure condition requires that

$$X_k + X'_k = X_k^0, \quad \text{a constant} \quad (16.1)$$

If X_k and X'_k are unconstrained, their equilibrium values are determined by the vanishing of the quantity

$$\mathcal{F}_k \equiv \left(\frac{\partial S^0}{\partial X_k} \right)_{X_k^0} = \left(\frac{\partial(S + S')}{\partial X_k} \right)_{X_k^0} = \frac{\partial S}{\partial X_k} - \frac{\partial S'}{\partial X'_k} = F_k - F'_k \quad (16.2)$$

Thus, if $\mathcal{F}_k$ is zero, the system is in equilibrium, but if $\mathcal{F}_k$ is nonzero an irreversible process occurs, taking the system toward the equilibrium state. The quantity $\mathcal{F}_k$, which is the difference in the entropy-representation intensive parameters, acts as a "generalized force" which "drives" the process. Such generalized forces are called *affinities*.

For definiteness, consider two systems separated by a diathermal wall, and let X_k be the energy U . Then the affinity is

$$\mathcal{F}_k = \frac{1}{T} - \frac{1}{T'} \quad (16.3)$$

No heat flows across the diathermal wall if the difference in inverse temperatures vanishes. But a nonzero difference in inverse temperature, acting as a generalized force, drives a flow of heat between the subsystems.

Similarly, if X_k is the volume, the affinity $\mathcal{F}_k$ is $[P/T - (P'/T')]$, and if X_k is a mole number the associated affinity is $[\mu_k/T' - (\mu_k/T)]$.

We characterize the response to the applied force by the rate of change of the extensive parameter X_k . The *flux* J_k is then defined by

$$J_k \equiv \frac{dX_k}{dt} \quad (16.4)$$

Therefore, the flux vanishes if the affinity vanishes, and a nonzero affinity leads to a nonzero flux. It is the relationship between fluxes and affinities that characterizes the rates of irreversible processes.

The identification of the affinities in a particular type of system is frequently rendered more convenient by considering the rate of production of entropy. Differentiating the entropy $S(X_0, X_1, \dots)$ with respect to the time, we have

$$\frac{dS}{dt} = \sum_k \frac{\partial S}{\partial X_k} \frac{dX_k}{dt} \quad (16.5)$$

or

$$\dot{S} = \sum_k \mathcal{F}_k J_k \quad (16.6)$$

Thus, the rate of production of entropy is the sum of products of each flux with its associated affinity.

The entropy production equation is particularly useful in extending the definition of affinities to continuous systems rather than to discrete systems. If heat flows from one homogeneous subsystem to another, through an infinitely thin diathermal partition, the generalized force is the difference $[1/T - (1/T')]$; but if heat flows along a metal rod, in which the temperature varies in a continuous fashion, it is difficult to apply our previous definition of the affinity. Nevertheless, we can compute the rate of production of entropy, and thereby we can identify the affinity.

With the foregoing considerations to guide us, we now turn our attention to continuous systems. We consider a three dimensional system in which energy and matter flow, driven by appropriate forces. As fluxes, we choose the components of the vector current densities of energy and matter. Thus, associated with the energy U , we have the three energy fluxes J_{ox} , J_{oy} , J_{oz} . These quantities are the x , y , and z components of the vector current density $\mathbf{J}_o$. By definition the magnitude of $\mathbf{J}_o$ is the amount of energy which flows across the unit area in unit time, and the direction of $\mathbf{J}_o$ is the direction of this energy flow. Similarly, the current density $\mathbf{J}_k$ may describe the flow of a particular chemical component per unit area and per unit time; the components J_{kx} , J_{ky} , and J_{kz} are fluxes.

In order to identify the affinities, we now seek to write the rate of production of entropy in a form analogous to equation 16.6.

One problem that immediately arises is that of defining entropy in a nonequilibrium system. This problem is solved in a formal manner as follows.

To any infinitesimal region we associate a local entropy $S(X_0, X_1 \dots)$, where, by definition, the functional dependence of S on the local extensive parameters $X_0, X_1 \dots$ is taken to be identical to the dependence in equilibrium. That is, we merely adopt the equilibrium fundamental equation to associate a local entropy with the local parameters $X_0, X_1 \dots$. Then

$$dS = \sum_k F_k dX_k \quad (16.7)$$

or, taking all quantities per unit volume,*

$$ds = \sum_k F_k dx_k \quad (16.8)$$

The summation in this equation omits the term for volume and consequently has one less term than that in equation 16.7.

Again, the local intensive parameter F_k is taken to be the same function of the local extensive parameters as it would be in equilibrium. It is because

* It should be noted that in the remainder of this chapter we use lower case letters to indicate extensive parameters per unit volume rather than per mole.

of this convention, incidentally, that we can speak of the temperature varying continuously in a bar, despite the fact that thermostatics implies the existence of temperature only in equilibrium systems.

Equation 16.7 immediately suggests a reasonable definition of the entropy current density $\mathbf{J}_S$.

$$\mathbf{J}_S = \sum F_k \mathbf{J}_k \quad (16.9)$$

in which $\mathbf{J}_k$ is the current density of the extensive parameter X_k . The magnitude of the entropy flux $\mathbf{J}_S$ is the entropy transported through unit area per unit time.

The rate of local production of entropy is equal to the entropy leaving the region, plus the rate of increase of entropy within the region. If $\dot{s}$ denotes the rate of production of entropy per unit volume and $\partial s / \partial t$ denotes the increase in entropy per unit volume, then

$$\dot{s} = \frac{\partial s}{\partial t} + \nabla \cdot \mathbf{J}_S \quad (16.10)$$

The various extensive parameters can be neither produced nor destroyed, so that the equations of continuity for these parameters become

$$0 = \frac{\partial x_k}{\partial t} + \nabla \cdot \mathbf{J}_k \quad (16.11)$$

We are now prepared to compute $\dot{s}$ explicitly and thence to identify the affinities in continuous systems.

The first term in equation 16.10 is easily computed from equation 16.8.

$$\frac{\partial s}{\partial t} = \sum_k F_k \frac{\partial x_k}{\partial t} \quad (16.12)$$

The second term in equation 16.10 is computed by taking the divergence of equation 16.9.

$$\nabla \cdot \mathbf{J}_S = \nabla \cdot \left(\sum_k F_k \mathbf{J}_k \right) = \sum_k \nabla F_k \cdot \mathbf{J}_k + \sum_k F_k \nabla \cdot \mathbf{J}_k \quad (16.13)$$

Thus equation 16.10 becomes

$$\dot{s} = \sum_k F_k \frac{\partial x_k}{\partial t} + \sum_k \nabla F_k \cdot \mathbf{J}_k + \sum_k F_k \nabla \cdot \mathbf{J}_k \quad (16.14)$$

Finally, by equation 16.11, we observe that the first and third terms cancel, giving

$$\dot{s} = \sum_k \nabla F_k \cdot \mathbf{J}_k \quad (16.15)$$

Although the affinity is defined as the difference in the entropy-representation

intensive parameters for discrete systems, it is the gradient of the entropy-representation intensive parameters in continuous systems.

If J_{oz} denotes the z component of the energy current density, the associated affinity $\mathcal{F}_{oz}$ is $\nabla_z(1/T)$, the z component of the gradient of the inverse temperature. And if J_k denotes the k th mole number current density (the number of moles of the k th component flowing through unit area per second), the affinity associated with J_{kz} is $\mathcal{F}_{kz} = -\nabla_z\left(\frac{\mu_k}{T}\right)$.

16.3 Markoffian Systems

For certain systems the fluxes at a given instant depend only on the values of the affinities at that instant. We call such systems *Markoffian*, borrowing the terminology from the theory of random processes, and we restrict our attention to this type of system.

For a non-Markoffian system the fluxes may depend upon the values of the affinities at previous times as well as upon the values at the present time. In the electrical case a pure resistor is a Markoffian system, whereas a circuit with capacitance or inductance is non-Markoffian. A non-Markoffian system has a "memory."

Although it might appear that the restriction to Markoffian systems is a very severe restriction indeed, it is found in practice that almost all systems of interest, other than electrical systems, are Markoffian. The extension of the theory to non-Markoffian systems, which we shall not present here, has been more important for its elucidation of principles than for its application to real systems.

For a Markoffian system, by definition, each local flux depends only upon the instantaneous local affinities and upon the local intensive parameters. That is, dropping the indices denoting vector components,

$$J_k = J_k(\mathcal{F}_0, \mathcal{F}_1 \cdots \mathcal{F}_j \cdots; F_0, F_1 \cdots F_j \cdots) \quad (16.16)$$

Thus, the local mole number current density of the k th component depends on the gradient of the inverse temperature, on the gradients of μ_j/T for each component, and upon the local temperature, pressure, etc. It should be noted that we do not assume that each flux depends only on its own affinity but rather that each flux depends on *all* affinities. It is true that each flux tends to depend most strongly on its own associated affinity, but the dependence of a flux on other affinities as well is the source of some of the most interesting phenomena in the field of irreversibility.

Each flux J_k is known to vanish as the affinities vanish, so we can expand J_k in powers of the affinities with no constant term.

$$J_k = \sum_j L_{jk} \mathcal{F}_j + \frac{1}{2!} \sum_i \sum_j L_{ijk} \mathcal{F}_i \mathcal{F}_j + \cdots \quad (16.17)$$

where

$$L_{jk} = \left(\frac{\partial J_k}{\partial \mathcal{F}_j} \right)_0 \quad (16.18)$$

and

$$L_{ijk} = \left(\frac{\partial^2 J_k}{\partial \mathcal{F}_i \partial \mathcal{F}_j} \right)_0 \quad (16.19)$$

The functions L_{jk} are called *kinetic coefficients*. They are functions of the local intensive parameters.

$$L_{jk} = L_{jk}(F_0, F_1 \cdots) \quad (16.20)$$

The functions L_{ijk} are called *second-order kinetic coefficients*, and they are also functions of the local intensive parameters. Third-order and higher-order kinetic coefficients are similarly defined.

For the purposes of the Onsager theorem, which we are about to enunciate, it is convenient to adopt a notation that exhibits the functional dependence of the kinetic coefficients on an externally applied magnetic field H_e , suppressing the dependence on the other intensive parameters.

$$L_{jk} = L_{jk}(H_e) \quad (16.21)$$

The Onsager theorem states that

$$L_{jk}(H_e) = L_{kj}(-H_e) \quad (16.22)$$

That is, the value of the kinetic coefficient L_{jk} measured in an external magnetic field H_e is identical to the value of L_{kj} measured in the reversed magnetic field $-H_e$.

The Onsager theorem states a symmetry between the linear effect of the j th affinity on the k th flux and the linear effect of the k th affinity on the j th flux when these effects are measured in opposite magnetic fields.

16.4 Linear Processes

A situation of great practical interest arises if the affinities are so small that all quadratic and higher-order terms in equation 16.17 can be neglected. A process that can be adequately described by the truncated approximate equations

$$J_k = \sum_j L_{jk} \mathcal{F}_j \quad (16.23)$$

is called a *linear* Markoff process. For the analysis of such processes the Onsager theorem is a particularly powerful tool.

It is perhaps surprising that so many physical processes of interest are linear. But the affinities that we commonly encounter in the laboratory are quite small in the sense of equation 16.17, and we therefore recognize that we generally deal with systems that deviate only slightly from equilibrium.

Phenomenologically, it is found that the flow of energy in a thermally conducting body is proportional to the gradient of the temperature. Denoting the energy current density by J_o , experiment yields the linear law

$$J_o = -\kappa \nabla T \quad (16.24)$$

in which κ is the thermal conductivity of the body. We can rewrite this in the more appropriate form

$$J_{oz} = \kappa T^2 \nabla_z \left(\frac{1}{T} \right) \quad (16.25)$$

and similarly for x and y components, and we see that (κT^2) is the kinetic coefficient. The absence of higher-order terms, such as $[\nabla(1/T)]^2$ and $[\nabla(1/T)]^3$, in the phenomenological law shows that commonly employed temperature gradients are small in the sense of equation 16.17.

Ohm's law of electrical conduction and Fick's law of diffusion are other linear phenomenological laws which demonstrate that for the common values of the affinities in these processes higher-order terms are negligible. On the other hand, both the linear region and the nonlinear region can be realized easily in chemical systems, depending upon the deviations of the molar concentrations from their equilibrium values. Although the class of linear processes is sufficiently common to merit special attention, it is by no means all-inclusive, and contrary to the usual statement the Onsager theorem is *not* restricted to this special class of systems.

16.5 The Statistical Basis of the Onsager Reciprocity

The Onsager reciprocity has been stated without proof in the preceding sections. Applications are made in Chapter 17. In this section we indicate the relationship of the Onsager reciprocity to the underlying principle of time symmetry of physical laws.

We consider a system in equilibrium, and we address our attention to the spontaneous fluctuations, as in Chapter 15. Consider, in particular, a correlation moment such as

$$\langle \delta \hat{X}_j, \delta \hat{X}_k(\tau) \rangle \quad (16.26)$$

which is the average product of the deviation $\delta \hat{X}_j$ and of the deviation $\delta \hat{X}_k$, the latter being observed a time τ after the former. Assuming, for simplicity, that no magnetic field is present, the principle of time symmetry requires that the correlation moment (16.26) be unchanged if we replace τ by $-\tau$.

$$\langle \delta \hat{X}_j, \delta \hat{X}_k(\tau) \rangle = \langle \delta \hat{X}_j, \delta \hat{X}_k(-\tau) \rangle \quad (16.27)$$

or, since only the relative times in the two factors are significant,

$$\langle \delta \hat{X}_j, \delta \hat{X}_k(\tau) \rangle = \langle \delta \hat{X}_j(\tau), \delta \hat{X}_k \rangle \quad (16.28)$$

If we now subtract $\langle \delta \hat{X}_j, \delta \hat{X}_k \rangle$ from each side of the equation and divide by τ , we find

$$\left\langle \delta \hat{X}_j, \frac{\delta \hat{X}_k(\tau) - \delta \hat{X}_k}{\tau} \right\rangle = \left\langle \frac{\delta \hat{X}_j(\tau) - \delta \hat{X}_j}{\tau}, \delta \hat{X}_k \right\rangle \quad (16.29)$$

In the limit as $\tau \rightarrow 0$ we can write the foregoing equation in terms of time derivatives.

$$\langle \delta \hat{X}_j, \delta \hat{X}_k \rangle = \langle \delta \hat{X}_j, \delta \hat{X}_k \rangle \quad (16.30)$$

Now, we *assume* that the decay of a fluctuation $\delta \hat{X}_k$ is governed by the *same* linear dynamical laws as are macroscopic processes.

$$\delta \hat{X}_k = \sum_i L_{ik} \delta \hat{\mathcal{F}}_i \quad (16.31)$$

Inserting these equations in equation 16.30 gives

$$\sum_i L_{ik} \langle \delta \hat{X}_j, \delta \hat{\mathcal{F}}_i \rangle = \sum_i L_{ij} \langle \delta \hat{\mathcal{F}}_i, \delta \hat{X}_k \rangle \quad (16.32)$$

However, we shall show below, by the methods of Chapter 15, that

$$\langle \delta \hat{X}_j, \delta \hat{\mathcal{F}}_i \rangle = \begin{cases} -k & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases} \quad (16.33)$$

in which k is Boltzmann's constant. Thus equation 16.32 becomes

$$L_{ij} = L_{ji} \quad (16.34)$$

which is the Onsager theorem in the absence of a magnetic field.

To complete the proof we now demonstrate equation 16.33. From equation 15.1 we can write the distribution function for the spontaneous fluctuations in the form

$$W = \Omega \exp \frac{1}{k} (\delta \mathcal{S} - \sum_i F_i \delta \hat{X}_i) \quad (16.35)$$

Combining this with equation 15.4 indicates that

$$W \delta \hat{\mathcal{F}}_i = k \frac{\partial W}{\partial \delta X_i} \quad (16.36)$$

Consider now the average value in equation 16.33.

$$\langle \delta X_i, \delta \hat{\mathcal{F}}_i \rangle = \int \delta X_i, \delta \hat{\mathcal{F}}_i W d\delta X_1 d\delta X_2 \cdots \quad (16.37)$$

$$= k \int \delta X_i, \frac{\partial W}{\partial \delta X_i} d\delta X_1 d\delta X_2 \cdots \quad (16.38)$$

If $i \neq j$, the integral over $d\delta X_i$ vanishes at both limits. If $i = j$, we integrate by parts, immediately obtaining the result 16.33. An alternative, and easier, derivation of equation 16.33 is readily obtained on the basis of the approximate Gaussian distribution of section 15.6 rather than by the rigorous distribution used above. Such an alternative derivation is essentially given in problem 15.6-1.

Our derivation of the Onsager reciprocity is that given by Onsager. Extension to the case in which a magnetic field is present is quite simple. However, justification of the assumption that the macroscopic dynamical laws can be applied to the decay of a spontaneous fluctuation is not simple. Justification of this assumption requires rather powerful statistical mechanical analysis, so that this section should be viewed as a demonstration of plausibility rather than as a statistical mechanical derivation.

Thermoelectric and Thermomagnetic Effects

17.1 The Dynamical Equations

As applications of the Onsager theorem we shall consider the thermoelectric and thermomagnetic effects, which are phenomena associated with the simultaneous flow of electric current and heat in a system. These phenomena, and certain relations among them, were proposed in 1854 by Lord Kelvin on the basis of empirical observations. Kelvin also presented a suggestive argument leading to the relations, carefully pointing out, however, that the argument was not only unjustifiable but that it could be made to yield incorrect relations as well as correct ones. It is a curious fact that many modern thermodynamics texts still present Kelvin's argument as a rigorous proof, completely ignoring Kelvin's own admonition to the contrary and ignoring the methods of modern irreversibility theory.

As remarked above, the thermoelectric and thermomagnetic effects are phenomena associated with the simultaneous flow of heat and electric current in a system. For definiteness of expression we shall think of a solid in which the charge carriers are electrons. Then, if s is the local entropy density, we have

$$ds = \frac{1}{T} du - \frac{\mu}{T} dn - \sum_k \left(\frac{\mu_k}{T} \right) dn_k \quad (17.1)$$

in which u is the local energy density, μ is the electrochemical potential (per particle) of the electrons, n is the number of electrons per unit

volume, and in which the sum refers to other "components." These other components refer to the various types of atomic nuclei that together with the electrons constitute the solid. It will be noted that we have taken n as the number of electrons rather than the number of moles of electrons, and μ is accordingly the electrochemical potential per particle rather than per mole. In this regard we deviate from the more usual parameters merely by multiplication and division by Avogadro's number, respectively.

Just as equation 16.7 led to equation 16.9, equation 17.1 now leads to

$$J_S = \frac{1}{T} J_U - \frac{\mu}{T} J_N \quad (17.2)$$

in which J_S , J_U , and J_N are current densities of entropy, energy, and number of electrons, respectively. The other components in equation 17.1 are assumed immobile and consequently do not contribute flux terms to equation 17.2.

Repeating the logic leading to equation 16.15, we find

$$\dot{s} = \nabla \cdot \frac{1}{T} J_U - \nabla \cdot \frac{\mu}{T} J_N \quad (17.3)$$

Thus, if the components of J_U and $-J_N$ are taken as fluxes, the associated affinities are the components of $\nabla \frac{1}{T}$ and $\nabla \frac{\mu}{T}$. Assuming for simplicity that all flows and forces are parallel to the x -direction, and omitting the subscript x , the linear dynamical laws become

$$-J_N = L'_{11} \nabla \frac{\mu}{T} + L'_{12} \nabla \frac{1}{T} \quad (17.4)$$

$$J_U = L'_{21} \nabla \frac{\mu}{T} + L'_{22} \nabla \frac{1}{T} \quad (17.5)$$

and the Onsager theorem gives the relation

$$L'_{12}(H_e) = L'_{21}(-H_e) \quad (17.6)$$

In writing the foregoing dynamical equations we have assumed one-dimensional flow, such as occurs in wires or bars. This is the case of interest to us in the analysis of the thermoelectric effects. When we consider the thermomagnetic effects in section 17.6, however, we shall have to take explicit cognizance of the fact that the kinetic coefficients for the x -directed currents may differ from the kinetic coefficients for the y -directed currents.

Before drawing physical conclusions from equation 17.6, we recast the dynamical equations into an equivalent but instructive form. Although

J_U is a current density of total internal energy, we generally prefer to discuss the current density of heat. In analogy with the relation $dQ = T dS$ we therefore define a heat current density J_Q by the relation

$$J_Q = T J_S \quad (17.7)$$

or, by equation 17.2,

$$J_Q = J_U - \mu J_N \quad (17.8)$$

In a very rough intuitive way we can look on μ as the potential energy per particle and on μJ_N as a current density of potential energy; subtraction of the potential energy current density from the total energy current density yields the heat current density as a sort of kinetic energy current density. At any rate, eliminating J_U in favor of J_Q from equation 17.3 gives

$$\dot{s} = \nabla \cdot \frac{1}{T} J_Q - \frac{1}{T} \nabla \mu \cdot J_N \quad (17.9)$$

It follows from this equation that if the components of J_Q and of $-J_N$ are chosen as fluxes the associated affinities are the corresponding components of $\nabla(1/T)$ and of $(1/T)\nabla\mu$, respectively. The dynamical equations can then be written, in the one-dimensional case, as

$$-J_N = L_{11} \frac{1}{T} \nabla \mu + L_{12} \nabla \frac{1}{T} \quad (17.10)$$

$$J_Q = L_{21} \frac{1}{T} \nabla \mu + L_{22} \nabla \frac{1}{T} \quad (17.11)$$

and the Onsager relation is

$$L_{12}(H_e) = L_{21}(-H_e) \quad (17.12)$$

The reader should verify that the dynamical equations 17.10 and 17.11 can also be obtained by direct substitution of equation 17.8 into the previous pair of dynamical equations 17.4 and 17.5 without recourse to the entropy production equation 17.9.

The significance of the heat current can be exhibited in another manner. We consider, for a moment, a steady-state flow. Then both J_U and J_N are divergenceless and taking the divergence of equation 17.8 gives

$$\nabla \cdot J_Q = -\nabla \mu \cdot J_N \quad (\text{in the steady state}) \quad (17.13)$$

which states that in the steady state the rate of increase in heat current is equal to the rate of decrease in the potential energy current. Furthermore, the insertion of this equation into equation 17.9 gives

$$\dot{s} = \nabla \cdot \frac{1}{T} J_Q + \frac{1}{T} \nabla \cdot J_Q \quad (17.14)$$

which can be interpreted as stating that the production of entropy is due to two causes; the first term is the production of entropy due to the flow of heat from high to low temperature, and the second term is the increase in entropy due to the appearance of heat current.

We now accept the dynamical equations 17.10 and 17.11 and the symmetry condition (equation 17.12) as the basic equations with which to study the flow of heat and electric current in a system.

17.2 The Conductivities

We consider a system in which an electric current and a heat current flow parallel to the x -axis in a steady state, with no applied magnetic field. Then, omitting the subscript x ,

$$-J_N = L_{11} \frac{1}{T} \nabla \mu + L_{12} \nabla \frac{1}{T} \quad (17.15)$$

$$J_Q = L_{12} \frac{1}{T} \nabla \mu + L_{22} \nabla \frac{1}{T} \quad (17.16)$$

where the Onsager theorem has reduced to the simple symmetry

$$L_{12} = L_{21} \quad (17.17)$$

The three kinetic coefficients appearing in the dynamical equations can be related to more familiar quantities, such as conductivities. In developing this connection we first comment briefly on the nature of the electrochemical potential μ of the electrons. We can consider μ as composed of two parts, a chemical portion μ_e and an electrical portion μ_s ,

$$\mu = \mu_e + \mu_s \quad (17.18)$$

If the charge on an electron is e , then μ_s is simply $e\phi$, where ϕ is the ordinary electrostatic potential. The chemical potential μ_e is a function of the temperature and of the electron concentration. Restating these facts in terms of gradients, the electrochemical potential *per unit charge* is $(1/e)\mu$; its gradient $(1/e)\nabla\mu$ is the sum of the *electric field* $(1/e)\nabla\mu_e$, plus an effective driving force $(1/e)\nabla\mu_s$ arising from a concentration gradient.

The *electric conductivity* σ is defined as the electric current density (eJ_N) per unit potential gradient $(1/e)\nabla\mu$ in an isothermal system. It is easily seen that $(1/e)\nabla\mu$ is actually the emf, for in a homogeneous

isothermal system $\nabla\mu_e = 0$ and $\nabla\mu = \nabla\mu_s$. Thus, by definition,

$$\sigma \equiv -eJ_N / \frac{1}{e} \nabla\mu \quad \text{for} \quad \nabla T = 0 \quad (17.19)$$

whence equation 17.15 gives

$$\sigma = e^2 L_{11} / T \quad (17.20)$$

Similarly the *heat conductivity* κ is defined as the heat current density per unit temperature gradient for zero electric current.

$$\kappa \equiv -J_Q / \nabla T \quad \text{for} \quad J_N = 0 \quad (17.21)$$

Solving the two kinetic equations simultaneously, we find

$$\kappa = \frac{D}{T^2 L_{11}} \quad (17.22)$$

where D denotes the determinant of the kinetic coefficients

$$D \equiv L_{11} L_{22} - L_{12}^2 \quad (17.23)$$

17.3 The Seebeck Effect and the Thermoelectric Power

The Seebeck effect refers to the production of an electromotive force in a thermocouple under conditions of zero electric current.

Consider a thermocouple with junctions at temperatures T_1 and T_2 ($T_2 > T_1$), as indicated in Figure 17.1. A voltmeter is inserted in one arm of the thermocouple at a point at which the temperature is T' . This voltmeter is such that it allows no passage of electric current but offers no resistance to the flow of heat. We designate the two materials composing the thermocouple by A and B . With $J_N = 0$, we obtain from the kinetic equations, for either conductor,

$$\nabla\mu = \frac{L_{12}}{TL_{11}} \nabla T \quad (17.24)$$

Thus

$$\mu_2 - \mu_1 = \int_1^2 \frac{L_{12}^A}{TL_{11}^A} dT \quad (17.25)$$

$$\mu_2 - \mu'_r = \int_r^2 \frac{L_{12}^B}{TL_{11}^B} dT \quad (17.26)$$

$$\mu'_r - \mu_1 = \int_1^r \frac{L_{12}^B}{TL_{11}^B} dT \quad (17.27)$$

Eliminating μ_1 and μ_2 from these equations,

$$\mu'_r - \mu'_i = \int_1^2 \left(\frac{L_{12}^A}{TL_{11}^A} - \frac{L_{12}^B}{TL_{11}^B} \right) dT \quad (17.28)$$

But, because there is no temperature difference across the voltmeter, the voltage is simply

$$V = \frac{1}{e} (\mu'_r - \mu'_i) = \int_1^2 \left(\frac{L_{12}^A}{eTL_{11}^A} - \frac{L_{12}^B}{eTL_{11}^B} \right) dT \quad (17.29)$$

The *thermoelectric power* of the thermocouple, ϵ_{AB} , is defined as the change in voltage per unit change in temperature difference. The sign of

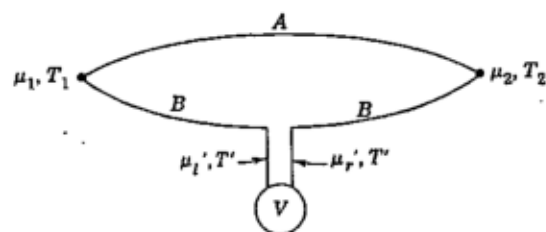


Figure 17.1

ϵ_{AB} is chosen as positive if the voltage increment is such as to drive the current from *A* to *B* at the hot junction. Then

$$\epsilon_{AB} = \frac{\partial V}{\partial T_2} = \left(\frac{-L_{12}^B}{eTL_{11}^B} \right) - \left(\frac{-L_{12}^A}{eTL_{11}^A} \right) \quad (17.30)$$

Defining the *absolute thermoelectric power* of a single medium by the relation

$$\epsilon_A \equiv \frac{-L_{12}^A}{eTL_{11}^A} \quad (17.31)$$

the thermoelectric power of the thermocouple is

$$\epsilon_{AB} = \epsilon_B - \epsilon_A \quad (17.32)$$

If we accept the electric conductivity σ , the heat conductivity κ , and the absolute thermoelectric power ϵ as the three physically significant dynamical properties of a medium, we can eliminate the three kinetic coefficients in favor of these quantities and rewrite the kinetic equations in the following form:

$$-J_N = \left(\frac{T\sigma}{e^2} \right) \frac{1}{T} \nabla \mu - \left(\frac{T^2 \sigma \epsilon}{e} \right) \nabla \frac{1}{T} \quad (17.33)$$

$$J_Q = - \left(\frac{T^2 \sigma \epsilon}{e} \right) \frac{1}{T} \nabla \mu + (T^3 \sigma \epsilon^2 + T^2 \kappa) \nabla \frac{1}{T} \quad (17.34)$$

An interesting insight to the physical meaning of the absolute thermoelectric power can be obtained by eliminating $(1/T) \nabla \mu$ between the two foregoing dynamical equations and writing J_Q in terms of J_N and $\nabla(1/T)$:

$$J_Q = T\epsilon e J_N + T^2 \kappa \nabla \frac{1}{T} \quad (17.35)$$

or, recalling that $J_S = J_Q/T$,

$$J_S = \epsilon e J_N + T \kappa \nabla \frac{1}{T} \quad (17.36)$$

According to this equation, each electron involved in the electric current carries with it an entropy of ϵe . This flow of entropy is in addition to the entropy current $T \kappa \nabla(1/T)$, which is independent of the electronic current. The thermoelectric power can be looked on as the entropy transported per coulomb by the electron flow.

17.4 The Peltier Effect

The Peltier effect refers to the evolution of heat accompanying the flow of an electric current across an isothermal junction of two materials. Consider an isothermal junction of two conductors *A* and *B* and an electric current eJ_N to flow as indicated in Figure 17.2. Then the total energy



Figure 17.2

current will be discontinuous across the junction, and the energy difference appears as *Peltier heat* at the junction. We have $J_U = J_Q + \mu J_N$, and since both μ and J_N are continuous across the junction it follows that the discontinuity in J_U is equal to the discontinuity in J_Q .

$$J_U^A - J_U^B = J_Q^A - J_Q^B \quad (17.37)$$

Because of the isothermal condition the dynamical equations 17.33 and 17.34 give, in either conductor,

$$J_Q = T\epsilon(eJ_N) \quad (17.38)$$

whence

$$J_Q^B - J_Q^A = T(\epsilon_B - \epsilon_A)(eJ_N) \quad (17.39)$$

The *Peltier coefficient* π_{AB} is defined as the heat that must be supplied to the junction when unit electric current passes from conductor *A* to conductor *B*. Thus

$$\pi_{AB} \equiv (J_Q^B - J_Q^A)/eJ_N = T(\epsilon_B - \epsilon_A) \quad (17.40)$$

Equation 17.40, which relates the Peltier coefficient to the absolute thermoelectric powers, is one of the relations presented on empirical evidence by Kelvin in 1854. It is called the *second Kelvin relation*.

The method by which we have derived equation 17.40 is typical of all applications of the Onsager relations, so that it may be appropriate to review the procedure. We first write the linear dynamical equations, reducing the number of kinetic coefficients appearing therein by invoking the Onsager relations. We then proceed to analyze various effects, expressing each in terms of the kinetic coefficients. When we have analyzed as many effects as there are kinetic coefficients, we rewrite the dynamical equations in terms of those effects rather than in terms of the kinetic coefficients (as in equations 17.33 and 17.34). Thereafter every additional effect analyzed on the basis of the dynamical equations results in a relation analogous to equation 17.40 and expresses this new effect in terms of the coefficients in the dynamical equation.

17.5 The Thomson Effect

The Thomson effect refers to the evolution of heat as an electric current traverses a temperature gradient in a material.

Consider a conductor carrying a heat current but no electric current. A temperature distribution governed by the temperature dependence of the kinetic coefficients will be set up. Let the conductor now be placed in contact at each point with a heat reservoir of the same temperature as that point, so that there is no heat interchange between conductor and reservoirs. Now let an electric current pass through the conductor. An interchange of heat will take place between conductor and reservoirs. This heat exchange consists of two parts—the *Joule heat* and the *Thomson heat*.

As the electric current passes along the conductor, any change in total energy flow must be supplied by an energy interchange with the reservoirs. Thus we must compute $\nabla \cdot \mathbf{J}_U$.

$$\nabla \cdot \mathbf{J}_U = \nabla \cdot (\mathbf{J}_Q + \mu \mathbf{J}_N) = \nabla \cdot \mathbf{J}_Q + \nabla \mu \cdot \mathbf{J}_N \quad (17.41)$$

which can be expressed in terms of $\mathbf{J}_N$ and $\nabla(1/T)$ by using equations 17.35 and 17.33.

$$\nabla \cdot \mathbf{J}_U = \nabla \cdot \left(T \epsilon \mathbf{J}_N + T^2 \kappa \nabla \frac{1}{T} \right) + \left(-\frac{e^2}{\sigma} \mathbf{J}_N + T^2 e \epsilon \nabla \frac{1}{T} \right) \cdot \mathbf{J}_N \quad (17.42)$$

or

$$\nabla \cdot \mathbf{J}_U = T \nabla \epsilon \cdot (e \mathbf{J}_N) + \nabla \cdot \left(T^2 \kappa \nabla \frac{1}{T} \right) - \frac{e^2}{\sigma} \mathbf{J}_N^2 \quad (17.43)$$

However the temperature distribution is that which is determined by the steady state with no electric current, and we know that $\nabla \cdot \mathbf{J}_U$ vanishes in that state. By putting $\mathbf{J}_N = 0$ and $\nabla \cdot \mathbf{J}_U = 0$ in equation 17.43, we conclude that the temperature distribution is such as to make the second term vanish, and consequently

$$\nabla \cdot \mathbf{J}_U = T \nabla \epsilon \cdot (e \mathbf{J}_N) - \frac{1}{\sigma} (e \mathbf{J}_N)^2 \quad (17.44)$$

Furthermore, noting that the thermoelectric power is a function of the local temperature, we write

$$\nabla \epsilon = \frac{d\epsilon}{dT} \nabla T \quad (17.45)$$

and

$$\nabla \cdot \mathbf{J}_U = T \frac{d\epsilon}{dT} \nabla T \cdot (e \mathbf{J}_N) - \frac{1}{\sigma} (e \mathbf{J}_N)^2 \quad (17.46)$$

The second term is the Joule heat, produced by the flow of electric current, even in the absence of a temperature gradient. The first term represents the Thomson heat, absorbed from the heat reservoirs when the current $e \mathbf{J}_N$ traverses the temperature gradient ∇T . The Thomson coefficient τ is defined as the Thomson heat absorbed per unit electric current and per unit temperature gradient.

$$\tau \equiv \frac{\text{Thomson heat}}{\nabla T \cdot (e \mathbf{J}_N)} = T \frac{d\epsilon}{dT} \quad (17.47)$$

Although we have obtained the foregoing relation between τ and ϵ by our standard procedure, it is of interest that this relation can be derived by an alternate procedure, combining the *second Kelvin relation* (equation 17.40) with considerations of energy conservation.

To carry out this alternate derivation, we consider a thermocouple subjected to a very small temperature difference dT . Into one arm of this thermocouple is inserted a battery of just such a voltage as to negate the Seebeck voltage, causing no electric current to flow in the thermocouple circuit.

In accordance with equations 17.30 and 17.32, the required emf of the battery is $\epsilon_B - \epsilon_A$. The thermocouple circuit is indicated in Figure 17.3.

We now consider the virtual transfer of a unit of charge around the circuit, and we list the various energy transfers that take place in the process. As the charge crosses the cold junction, from B to A , a Peltier heat of $+\pi_{BA}$ is absorbed from the reservoir. As the charge traverses the leg A of the thermocouple, the Thomson heat $\tau_A dT$ is absorbed from the

reservoirs. However, we ignore the Joule heat because we assume the charge to be transported so slowly that the Joule heat, which is quadratic in the currents, is negligible compared to the Thomson heat, which is linear in the currents. In traversing the hot junction from A to B the Peltier heat $\pi_{AB}(T + dT)$ is absorbed. In traversing the leg B the Thomson heat $-\tau_B dT$ is absorbed. And in traversing the battery an amount of

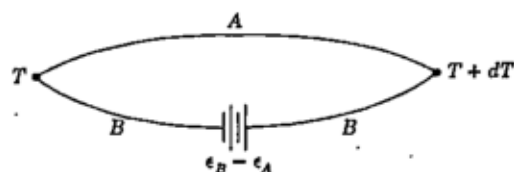


Figure 17.3

work equal to the emf of the battery, or $\epsilon_B - \epsilon_A$, is performed. Equating the total energy absorbed to the work done on the battery gives

$$\pi_{BA}(T) + \tau_A dT + \pi_{AB}(T + dT) - \tau_B dT = (\epsilon_B - \epsilon_A) dT \quad (17.48)$$

But

$$\pi_{AB}(T + dT) = \pi_{AB}(T) + \frac{d\pi_{AB}}{dT} dT \quad (17.49)$$

whence

$$\frac{d\pi_{AB}}{dT} + \tau_A - \tau_B = \epsilon_A - \epsilon_B \quad (17.50)$$

Finally, inserting equation 17.40 for the Peltier coefficient gives the equivalent of equation 17.47.

Equation 17.50, which depends on energy conservation alone and which does not require the Onsager theorem for its demonstration, was given by Kelvin and is called the *first Kelvin relation*.

17.6 The Thermomagnetic Dynamical Equations

Having demonstrated the technique of application of the Onsager theorem in some detail, we can now treat the thermomagnetic effects relatively concisely. These effects occur when electric and heat currents are permitted to flow in a plane perpendicular to an applied magnetic field, as shown in Figure 17.4.

The dynamical equations 17.10 and 17.11 apply specifically to one-dimensional flow. To obtain their analogues for two-dimensional flow, we return to equation 17.9, which we rewrite explicitly in its Cartesian

components. To simplify the notation we write N_x for J_{N_x} , Q_x for J_{Q_x} , and similarly for the y -components.

$$\dot{s} = \left(\nabla_x \frac{1}{T} \right) Q_x + \left(\nabla_y \frac{1}{T} \right) Q_y - \left(\frac{1}{T} \nabla_x \mu \right) N_x - \left(\frac{1}{T} \nabla_y \mu \right) N_y \quad (17.51)$$

where ∇_x denotes the partial derivative $\partial/\partial x$. We conclude that if $-N_x$, $-N_y$, Q_x , and Q_y are fluxes the associated affinities are $(1/T)\nabla_x \mu$,

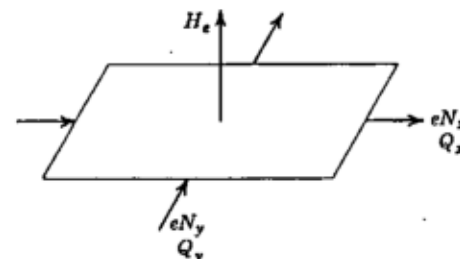


Figure 17.4

$(1/T)\nabla_y \mu$, $\nabla_x(1/T)$, and $\nabla_y(1/T)$, respectively. The dynamical equations then become

$$\begin{aligned} -N_x &= L'_{11} \frac{1}{T} \nabla_x \mu + L'_{12} \frac{1}{T} \nabla_y \mu + L'_{13} \nabla_x \frac{1}{T} + L'_{14} \nabla_y \frac{1}{T} \\ -N_y &= L'_{21} \frac{1}{T} \nabla_x \mu + L'_{22} \frac{1}{T} \nabla_y \mu + L'_{23} \nabla_x \frac{1}{T} + L'_{24} \nabla_y \frac{1}{T} \\ Q_x &= L'_{31} \frac{1}{T} \nabla_x \mu + L'_{32} \frac{1}{T} \nabla_y \mu + L'_{33} \nabla_x \frac{1}{T} + L'_{34} \nabla_y \frac{1}{T} \\ Q_y &= L'_{41} \frac{1}{T} \nabla_x \mu + L'_{42} \frac{1}{T} \nabla_y \mu + L'_{43} \nabla_x \frac{1}{T} + L'_{44} \nabla_y \frac{1}{T} \end{aligned} \quad (17.52)$$

The Onsager theorem states that

$$L'_{ij}(H_e) = L'_{ji}(-H_e) \quad (17.53)$$

If we assume isotropy in the xy -plane, the symmetry of the x - and y -axes requires that $L'_{11} = L'_{22}$, etc., reducing the dynamical equations to

$$\begin{aligned} -N_x &= L'_{11} \frac{1}{T} \nabla_x \mu + L'_{12} \frac{1}{T} \nabla_y \mu + L'_{13} \nabla_x \frac{1}{T} + L'_{14} \nabla_y \frac{1}{T} \\ -N_y &= L'_{12} \frac{1}{T} \nabla_x \mu + L'_{11} \frac{1}{T} \nabla_y \mu + L'_{14} \nabla_x \frac{1}{T} + L'_{13} \nabla_y \frac{1}{T} \\ Q_x &= L'_{31} \frac{1}{T} \nabla_x \mu + L'_{32} \frac{1}{T} \nabla_y \mu + L'_{33} \nabla_x \frac{1}{T} + L'_{34} \nabla_y \frac{1}{T} \\ Q_y &= -L'_{32} \frac{1}{T} \nabla_x \mu + L'_{31} \frac{1}{T} \nabla_y \mu - L'_{34} \nabla_x \frac{1}{T} + L'_{33} \nabla_y \frac{1}{T} \end{aligned} \quad (17.54)$$

in which, furthermore, L'_{11} , L'_{13} , L'_{31} , and L'_{33} are identified as even functions of the magnetic field, whereas L'_{12} , L'_{14} , L'_{32} , and L'_{34} are identified as odd functions of the magnetic field.

From the Onsager relation (equation 17.53) we now have

$$L'_{13}(H_e) = L'_{31}(-H_e) \quad (17.55)$$

However L'_{31} is an even function of the field, so that

$$L'_{31}(-H_e) = L'_{31}(H_e) \quad (17.56)$$

These two equations imply that

$$L'_{31}(H_e) = L'_{13}(H_e) \quad (17.57)$$

Similarly, from the Onsager relation,

$$L'_{14}(H_e) = L'_{41}(-H_e) \quad (17.58)$$

But examination of equations 17.54 shows that we have already identified L'_{41} as equal to $-L'_{32}$ by symmetry considerations, so that

$$L'_{14}(H_e) = -L'_{32}(-H_e) \quad (17.59)$$

Again, L'_{32} is an odd function of the magnetic field, implying finally that

$$L'_{14}(H_e) = L'_{32}(H_e) \quad (17.60)$$

The Onsager relation therefore enables us to eliminate two kinetic coefficients from the dynamical equations, which thereby become

$$\begin{aligned} -N_x &= L'_{11} \frac{1}{T} \nabla_x \mu + L'_{12} \frac{1}{T} \nabla_y \mu + L'_{13} \nabla_x \frac{1}{T} + L'_{14} \nabla_y \frac{1}{T} \\ -N_y &= -L'_{12} \frac{1}{T} \nabla_x \mu + L'_{11} \frac{1}{T} \nabla_y \mu - L'_{14} \nabla_x \frac{1}{T} + L'_{13} \nabla_y \frac{1}{T} \\ Q_x &= L'_{13} \frac{1}{T} \nabla_x \mu + L'_{14} \frac{1}{T} \nabla_y \mu + L'_{33} \nabla_x \frac{1}{T} + L'_{34} \nabla_y \frac{1}{T} \\ Q_y &= -L'_{14} \frac{1}{T} \nabla_x \mu + L'_{13} \frac{1}{T} \nabla_y \mu - L'_{34} \nabla_x \frac{1}{T} + L'_{33} \nabla_y \frac{1}{T} \end{aligned} \quad (17.61)$$

We are now prepared to undertake our analysis of the various thermomagnetic effects in principle. There are six kinetic coefficients in the dynamical equations. By introducing six effects and defining six descriptive coefficients for those effects, we can eliminate the kinetic coefficients in favor of these six descriptive coefficients. Any further effects analyzed will result in relations analogous to the Kelvin relations. However, Mazur and Prigogine have shown that the algebra is greatly

simplified if we first invert the dynamical equations in such a way that the electrical current and temperature gradients, which are the experimentally controlled variables, appear on the right.

In carrying out the inversion of the dynamical equations it is convenient also to introduce explicitly the electric current eN_x and the electrochemical potential per unit charge $(1/e)\nabla_x \mu$ and to write the equations in terms of $\nabla_x T$ instead of $\nabla_x(1/T)$. The various resulting factors of $1/e$, e , and $-1/T^2$ are absorbed into the new kinetic coefficients. We thus obtain

$$\begin{aligned} -\frac{1}{e} \nabla_x \mu &= L_{11} e N_x + L_{12} e N_y - L_{13} \nabla_x T - L_{14} \nabla_y T \\ -\frac{1}{e} \nabla_y \mu &= -L_{12} e N_x + L_{11} e N_y + L_{14} \nabla_x T - L_{13} \nabla_y T \\ Q_x &= -TL_{13} e N_x - TL_{14} e N_y - L_{33} \nabla_x T - L_{34} \nabla_y T \\ Q_y &= TL_{14} e N_x - TL_{13} e N_y + L_{34} \nabla_x T - L_{33} \nabla_y T \end{aligned} \quad (17.62)$$

The new kinetic coefficients L_{ij} are, of course, fairly complicated functions of the old kinetic coefficients L'_{ij} . But the precise form of these relationships is of no consequence to us. The only significant fact is that the symmetry of the coefficients in equation 17.62 is implied by the symmetry of the coefficients in equation 17.61, as the reader may convince himself without recourse to detailed algebraic inversion of the equations.

17.7 The Thermomagnetic Effects

We now proceed with the definition of a number of effects and of their associated descriptive coefficients.

1. The Absolute Thermoelectric Power

In the presence of a magnetic field the definition of the absolute thermoelectric power is conveniently taken as

$$\epsilon \equiv \frac{1}{e} \nabla_x \mu / \nabla_x T \quad \text{with} \quad N_x = N_y = \nabla_y T = 0 \quad (17.63)$$

whence

$$\epsilon = L_{13} \quad (17.64)$$

2. The Isothermal Electric Conductivity

$$\sigma_i \equiv -e N_x / \frac{1}{e} \nabla_x \mu \quad \text{with} \quad \nabla_x T = \nabla_y T = N_y = 0 \quad (17.65)$$

whence

$$\sigma_t = 1/L_{11} \quad (17.66)$$

3. The Adiabatic Electric Conductivity

$$\sigma_a \equiv -eN_x / \frac{1}{e} \nabla_x \mu \quad \text{with} \quad \nabla_x T = Q_v = N_v = 0 \quad (17.67)$$

whence

$$\sigma_a = (L_{11} - TL_{13}^2/L_{33})^{-1} \quad (17.68)$$

4. The Isothermal Heat Conductivity

$$\kappa_i \equiv -Q_x / \nabla_x T \quad \text{with} \quad N_x = N_v = \nabla_v T = 0 \quad (17.69)$$

whence

$$\kappa_i = L_{33} \quad (17.70)$$

5. The Adiabatic Heat Conductivity

$$\kappa_a \equiv -Q_x / \nabla_x T \quad \text{with} \quad N_x = N_v = Q_v = 0 \quad (17.71)$$

whence

$$\kappa_a = (L_{33}^2 + L_{34}^2)/L_{33} \quad (17.72)$$

6. The Isothermal Hall Effect

$$R_i \equiv \frac{1}{e} \nabla_v \mu / H_e e N_x \quad \text{with} \quad \nabla_x T = \nabla_v T = N_v = 0 \quad (17.73)$$

whence

$$R_i = L_{12}/H_e \quad (17.74)$$

7. The Adiabatic Hall Effect

$$R_a \equiv \frac{1}{e} \nabla_v \mu / H_e e N_x \quad \text{with} \quad \nabla_x T = Q_v = N_v = 0 \quad (17.75)$$

whence

$$R_a = (L_{12} + TL_{13}L_{14}/L_{33})/H_e \quad (17.76)$$

8. The Isothermal Nernst Effect

$$\eta_i \equiv -\frac{1}{e} \nabla_v \mu / H_e \nabla_x T \quad \text{with} \quad N_x = N_v = \nabla_v T = 0 \quad (17.77)$$

whence

$$\eta_i = L_{14}/H_e \quad (17.78)$$

9. The Adiabatic Nernst Effect

$$\eta_a \equiv -\frac{1}{e} \nabla_v \mu / H_e \nabla_x T \quad \text{with} \quad N_x = N_v = Q_v = 0 \quad (17.79)$$

whence

$$\eta_a = (L_{14} - L_{13}L_{34}/L_{33})/H_e \quad (17.80)$$

10. The Ettingshausen Effect

$$E = \nabla_v T / H_e e N_x \quad \text{with} \quad N_v = Q_v = \nabla_x T = 0 \quad (17.81)$$

whence

$$E = TL_{14}/H_e L_{33} \quad (17.82)$$

11. The Leduc-Righi Effect

$$\mathcal{L} \equiv \nabla_v T / H_e \nabla_x T \quad \text{with} \quad N_x = N_v = Q_v = 0 \quad (17.83)$$

whence

$$\mathcal{L} = L_{34}/H_e L_{33} \quad (17.84)$$

The fundamental set of dynamical equations can now be written in the matrix form

$$\begin{bmatrix} -\frac{1}{e} \nabla_x \mu \\ -\frac{1}{e} \nabla_v \mu \\ Q_x \\ Q_v \end{bmatrix} = \begin{bmatrix} \sigma_i^{-1} & H_e R_i & -\epsilon & -H_e \eta_i \\ -H_e R_i & \sigma_i^{-1} & H_e \eta_i & -\epsilon \\ -T\epsilon & -TH_e \eta_i & -\kappa_i & -H_e \kappa_i \mathcal{L} \\ TH_e \eta_i & -T\epsilon & H_e \kappa_i \mathcal{L} & -\kappa_i \end{bmatrix} \begin{bmatrix} eN_x \\ eN_v \\ \nabla_x T \\ \nabla_v T \end{bmatrix} \quad (17.85)$$

We further find the relations

$$\kappa_i E = T\eta_i \quad (17.86)$$

$$\kappa_a - \kappa_i = H_e \kappa_i^2 \mathcal{L}^2 \quad (17.87)$$

$$\sigma_i^{-1} - \sigma_i^{-1} = H_e^2 \eta_i E \quad (17.88)$$

$$R_a - R_i = \epsilon E \quad (17.89)$$

$$\eta_i - \eta_a = \epsilon \mathcal{L} \quad (17.90)$$

Each of the coefficients is an even function of the magnetic field. Thus the isothermal conductivity can be expanded in powers of H_e to give

$$\sigma_i = \sigma_i^0 + \sigma_i^{(2)} H_e^2 + \sigma_i^{(4)} H_e^4 + \dots \quad (17.91)$$

and the coefficient of the quadratic term is called a *magneto-conductivity coefficient*.

Any experimental situation can be directly analyzed by equation 17.85, relating it to the thermomagnetic coefficients appearing therein. The resultant equations, analogous to the thermomagnetic relations 17.86-17.90, represent the fruits of the theory of irreversible processes applied to conductivity phenomena.

Some Relations Involving Partial Derivatives

A.1 Partial Derivatives

In thermodynamics we are interested in continuous functions of three (or more) variables.

$$\psi = \psi(x, y, z) \quad (\text{A.1})$$

If two independent variables, say y and z , are held constant, ψ becomes a function of only one independent variable x , and the derivative of ψ with respect to x may be defined and computed in the standard fashion. The derivative so obtained is called the *partial derivative* of ψ with respect to x and is denoted by the symbol $(\partial\psi/\partial x)_{y,z}$ or simply by $\partial\psi/\partial x$. The derivative depends upon x and also upon the values at which y and z are held during the differentiation; that is $\partial\psi/\partial x$ is a function of x , y , and z . The derivatives $\partial\psi/\partial y$ and $\partial\psi/\partial z$ are defined in an identical manner.

The function $\partial\psi/\partial x$, if continuous, may itself be differentiated to yield three derivatives which are called the *second partial derivatives* of ψ :

$$\begin{aligned} \frac{\partial}{\partial x} \left(\frac{\partial\psi}{\partial x} \right) &\equiv \frac{\partial^2\psi}{\partial x^2} \\ \frac{\partial}{\partial y} \left(\frac{\partial\psi}{\partial x} \right) &\equiv \frac{\partial^2\psi}{\partial y \partial x} \\ \frac{\partial}{\partial z} \left(\frac{\partial\psi}{\partial x} \right) &\equiv \frac{\partial^2\psi}{\partial z \partial x} \end{aligned} \quad (\text{A.2})$$

By partial differentiation of the functions $\partial\psi/\partial y$ and $\partial\psi/\partial z$, we obtain other second partial derivatives of ψ :

$$\frac{\partial^2\psi}{\partial x \partial y}, \quad \frac{\partial^2\psi}{\partial y^2}, \quad \frac{\partial^2\psi}{\partial z \partial y}, \quad \frac{\partial^2\psi}{\partial x \partial z}, \quad \frac{\partial^2\psi}{\partial y \partial z}, \quad \text{and} \quad \frac{\partial^2\psi}{\partial z^2}$$

It may be shown that under the continuity conditions which we have assumed for ψ and its partial derivatives the order of differentiation is immaterial, so that

$$\frac{\partial^2\psi}{\partial x \partial y} = \frac{\partial^2\psi}{\partial y \partial x}, \quad \frac{\partial^2\psi}{\partial x \partial z} = \frac{\partial^2\psi}{\partial z \partial x}, \quad \frac{\partial^2\psi}{\partial y \partial z} = \frac{\partial^2\psi}{\partial z \partial y} \quad (\text{A.3})$$

There are therefore just six nonequivalent second partial derivatives of a function of three independent variables (three for a function of two variables, and $\frac{1}{2}n(n+1)$ for a function of n variables).

A.2 Taylor's Expansion

The relationship between $\psi(x, y, z)$ and $\psi(x+dx, y+dy, z+dz)$, where dx, dy , and dz denote arbitrary increments in x, y , and z , is given by Taylor's expansion:

$$\begin{aligned} \psi(x+dx, y+dy, z+dz) &= \psi(x, y, z) + \left(\frac{\partial\psi}{\partial x} dx + \frac{\partial\psi}{\partial y} dy + \frac{\partial\psi}{\partial z} dz \right) \\ &+ \frac{1}{2} \left[\frac{\partial^2\psi}{\partial x^2} (dx)^2 + \frac{\partial^2\psi}{\partial y^2} (dy)^2 + \frac{\partial^2\psi}{\partial z^2} (dz)^2 + 2 \frac{\partial^2\psi}{\partial x \partial y} dx dy \right. \\ &\left. + 2 \frac{\partial^2\psi}{\partial x \partial z} dx dz + 2 \frac{\partial^2\psi}{\partial y \partial z} dy dz \right] + \dots \end{aligned} \quad (\text{A.4})$$

This expansion can be written in a convenient symbolic form:

$$\psi(x+dx, y+dy, z+dz) = e^{\left(dx \frac{\partial}{\partial x} + dy \frac{\partial}{\partial y} + dz \frac{\partial}{\partial z}\right)} \psi(x, y, z) \quad (\text{A.5})$$

Expansion of the symbolic exponential according to the usual series

$$e^x = 1 + x + \frac{1}{2!} x^2 + \dots + \frac{1}{n!} x^n + \dots \quad (\text{A.6})$$

then reproduces the Taylor expansion (equation A.4)

A.3 Differentials of ψ

The Taylor expansion (equation A.4) can also be written in the form

$$\begin{aligned} \psi(x+dx, y+dy, z+dz) - \psi(x, y, z) \\ = d\psi + \frac{1}{2!} d^2\psi + \dots + \frac{1}{n!} d^n\psi \dots \end{aligned} \quad (\text{A.7})$$

where

$$d\psi = \frac{\partial\psi}{\partial x} dx + \frac{\partial\psi}{\partial y} dy + \frac{\partial\psi}{\partial z} dz \quad (\text{A.8})$$

$$\begin{aligned} d^2\psi &= \frac{\partial^2\psi}{\partial x^2} (dx)^2 + \frac{\partial^2\psi}{\partial y^2} (dy)^2 + \frac{\partial^2\psi}{\partial z^2} (dz)^2 + 2 \frac{\partial^2\psi}{\partial x \partial y} dx dy \\ &+ 2 \frac{\partial^2\psi}{\partial x \partial z} dx dz + 2 \frac{\partial^2\psi}{\partial y \partial z} dy dz \end{aligned} \quad (\text{A.9})$$

and generally

$$d^n\psi = \left(dx \frac{\partial}{\partial x} + dy \frac{\partial}{\partial y} + dz \frac{\partial}{\partial z} \right)^n \psi(x, y, z) \quad (\text{A.10})$$

These quantities $d\psi, d^2\psi, \dots, d^n\psi, \dots$ are called the *first, second, and n th order differentials* of ψ .

A.4 Composite Functions

Returning to the first-order differential,

$$d\psi = \left(\frac{\partial\psi}{\partial x} \right)_{y,z} dx + \left(\frac{\partial\psi}{\partial y} \right)_{x,z} dy + \left(\frac{\partial\psi}{\partial z} \right)_{x,y} dz \quad (\text{A.11})$$

an interesting case arises when x, y , and z are not varied independently but are themselves considered to be functions of some variable u . Then

$$dx = \frac{dx}{du} du, \quad dy = \frac{dy}{du} du \quad \text{and} \quad dz = \frac{dz}{du} du$$

whence

$$d\psi = \left[\left(\frac{\partial\psi}{\partial x} \right)_{y,z} \frac{dx}{du} + \left(\frac{\partial\psi}{\partial y} \right)_{x,z} \frac{dy}{du} + \left(\frac{\partial\psi}{\partial z} \right)_{x,y} \frac{dz}{du} \right] du \quad (\text{A.12})$$

or

$$\frac{d\psi}{du} = \left(\frac{\partial\psi}{\partial x} \right)_{y,z} \frac{dx}{du} + \left(\frac{\partial\psi}{\partial y} \right)_{x,z} \frac{dy}{du} + \left(\frac{\partial\psi}{\partial z} \right)_{x,y} \frac{dz}{du} \quad (\text{A.13})$$

If x and y are function of two (or more) variables, say u and v , then

$$dx = \left(\frac{\partial x}{\partial u} \right)_v du + \left(\frac{\partial x}{\partial v} \right)_u dv, \quad \text{etc.}$$

and

$$\begin{aligned} d\psi &= \left[\left(\frac{\partial\psi}{\partial x} \right)_{y,z} \left(\frac{\partial x}{\partial u} \right)_v + \left(\frac{\partial\psi}{\partial y} \right)_{x,z} \left(\frac{\partial y}{\partial u} \right)_v + \left(\frac{\partial\psi}{\partial z} \right)_{x,y} \left(\frac{\partial z}{\partial u} \right)_v \right] du \\ &+ \left[\left(\frac{\partial\psi}{\partial x} \right)_{y,z} \left(\frac{\partial x}{\partial v} \right)_u + \left(\frac{\partial\psi}{\partial y} \right)_{x,z} \left(\frac{\partial y}{\partial v} \right)_u + \left(\frac{\partial\psi}{\partial z} \right)_{x,y} \left(\frac{\partial z}{\partial v} \right)_u \right] dv \end{aligned} \quad (\text{A.14})$$

or

$$d\psi = \left(\frac{\partial\psi}{\partial u}\right)_v du + \left(\frac{\partial\psi}{\partial v}\right)_u dv \quad (\text{A.15})$$

where

$$\left(\frac{\partial\psi}{\partial u}\right)_v = \left(\frac{\partial\psi}{\partial x}\right)_{v,z} \left(\frac{\partial x}{\partial u}\right)_v + \left(\frac{\partial\psi}{\partial y}\right)_{v,z} \left(\frac{\partial y}{\partial u}\right)_v + \left(\frac{\partial\psi}{\partial z}\right)_{v,z} \left(\frac{\partial z}{\partial u}\right)_v \quad (\text{A.16})$$

and similarly for $(\partial\psi/\partial v)_u$.

It may happen that u is identical to x itself. Then

$$\left(\frac{\partial\psi}{\partial x}\right)_v = \left(\frac{\partial\psi}{\partial x}\right)_{v,z} + \left(\frac{\partial\psi}{\partial y}\right)_{v,z} \left(\frac{\partial y}{\partial x}\right)_v + \left(\frac{\partial\psi}{\partial z}\right)_{v,z} \left(\frac{\partial z}{\partial x}\right)_v \quad (\text{A.17})$$

Other special cases can be treated similarly.

A.5 Implicit Functions

If ψ is held constant, the variations of x , y , and z are not independent, and the relation

$$\psi(x, y, z) = \text{constant} \quad (\text{A.18})$$

gives an implicit functional relation among x , y , and z . This relation may be solved for one variable, say z , in terms of the other two.

$$z = z(x, y) \quad (\text{A.19})$$

This function can then be treated by the techniques described above to derive certain relations among the partial derivatives. However, a more direct method of obtaining the appropriate relations among the partial derivatives is merely to put $d\psi = 0$ in equation A.8.

$$0 = \left(\frac{\partial\psi}{\partial x}\right)_{v,z} dx + \left(\frac{\partial\psi}{\partial y}\right)_{x,z} dy + \left(\frac{\partial\psi}{\partial z}\right)_{x,y} dz \quad (\text{A.20})$$

If we now put $dz = 0$ and divide through by dx , we find

$$0 = \left(\frac{\partial\psi}{\partial x}\right)_{v,z} + \left(\frac{\partial\psi}{\partial y}\right)_{x,z} \left(\frac{\partial y}{\partial x}\right)_{v,z} \quad (\text{A.21})$$

in which the symbol $(\partial y/\partial x)_{v,z}$ appropriately indicates that the implied functional relation between y and x is that determined by the constancy of ψ and z . Equation A.21 can be written in the convenient form

$$\left(\frac{\partial y}{\partial x}\right)_{v,z} = -\frac{(\partial\psi/\partial x)_{v,z}}{(\partial\psi/\partial y)_{x,z}} \quad (\text{A.22})$$

This equation plays a very prominent role in thermodynamic calculations.

By successively putting $dy = 0$ and $dx = 0$ in equation A.20, we find the two similar relations

$$\left(\frac{\partial z}{\partial x}\right)_{v,y} = -\frac{(\partial\psi/\partial x)_{v,z}}{(\partial\psi/\partial z)_{x,y}} \quad (\text{A.23})$$

and

$$\left(\frac{\partial z}{\partial y}\right)_{v,x} = -\frac{(\partial\psi/\partial y)_{x,z}}{(\partial\psi/\partial z)_{x,y}} \quad (\text{A.24})$$

Returning to equation A.20 we again put $dz = 0$, but we now divide through by dy rather than by dx .

$$0 = \left(\frac{\partial\psi}{\partial x}\right)_{v,z} \left(\frac{\partial x}{\partial y}\right)_{v,z} + \left(\frac{\partial\psi}{\partial y}\right)_{x,z} \quad (\text{A.25})$$

whence

$$\left(\frac{\partial x}{\partial y}\right)_{v,z} = -\frac{(\partial\psi/\partial y)_{x,z}}{(\partial\psi/\partial x)_{v,z}} \quad (\text{A.26})$$

and, on comparison with equation A.21, we find the very reasonable result that

$$\left(\frac{\partial x}{\partial y}\right)_{v,z} = \frac{1}{(\partial y/\partial x)_{v,z}} \quad (\text{A.27})$$

From equations A.22–A.24 we then find

$$\left(\frac{\partial x}{\partial y}\right)_{v,z} \left(\frac{\partial y}{\partial z}\right)_{v,x} \left(\frac{\partial z}{\partial x}\right)_{v,y} = -1 \quad (\text{A.28})$$

Finally we return to our basic equation, which defines the differential $d\psi$, and consider the case in which x , y , and z are themselves functions of a variable u (as in equation A.12)

$$d\psi = \left[\left(\frac{\partial\psi}{\partial x}\right)_{v,z} \frac{dx}{du} + \left(\frac{\partial\psi}{\partial y}\right)_{x,z} \frac{dy}{du} + \left(\frac{\partial\psi}{\partial z}\right)_{x,y} \frac{dz}{du}\right] du \quad (\text{A.29})$$

If ψ is to be constant, there must be a relation among x , y , and z , hence also among dx/du , dy/du , and dz/du . We find

$$0 = \left(\frac{\partial\psi}{\partial x}\right)_{v,z} \left(\frac{dx}{du}\right)_v + \left(\frac{\partial\psi}{\partial y}\right)_{x,z} \left(\frac{dy}{du}\right)_v + \left(\frac{\partial\psi}{\partial z}\right)_{x,y} \left(\frac{dz}{du}\right)_v \quad (\text{A.30})$$

If we further require that z shall be a constant independent of u we find

$$0 = \left(\frac{\partial\psi}{\partial x}\right)_{v,z} \left(\frac{\partial x}{\partial u}\right)_{v,z} + \left(\frac{\partial\psi}{\partial y}\right)_{x,z} \left(\frac{\partial y}{\partial u}\right)_{v,z} \quad (\text{A.31})$$

or

$$\frac{(\partial y/\partial u)_{v,z}}{(\partial x/\partial u)_{v,z}} = -\frac{(\partial\psi/\partial x)_{v,z}}{(\partial\psi/\partial y)_{x,z}} \quad (\text{A.32})$$

Comparison with equation A.22 shows that

$$\left(\frac{\partial y}{\partial x}\right)_{v,z} = \frac{(\partial y/\partial u)_{v,z}}{(\partial x/\partial u)_{v,z}} \quad (\text{A.33})$$

Equations A.22, A.27, and A.33 are among the most useful formal manipulations in thermodynamic calculations.

Statistical Significance of the Entropy

The purpose of this appendix is to provide the reader with a descriptive, intuitive insight to the statistical significance of the entropy. An appreciation of the qualitative meaning of the entropy at the atomic level gives valuable perspective to macroscopic thermodynamic theory.

In Chapter 1 it is pointed out that each macroscopic system possesses an enormous number of atomic coordinates. Transitions among different atomic states occur extremely rapidly, whereas macroscopic observations are relatively slow. Macroscopic observations consequently correspond to statistical averages over the atomic coordinates.

Among the myriads of atomic coordinates there exist a very few with such symmetry and coherence properties that, unlike the vast majority, they are not "averaged out" in a macroscopic measurement. These coordinates are the energy, volume, mole numbers, and other macroscopic thermodynamic extensive parameters. The observed values of these parameters characterize a thermodynamic state or a *macrostate* of a system. Each such macrostate is, then, consistent with a very large number of *microstates*, or underlying atomic states.

As an example, consider two simple systems contained within a closed cylinder and separated by an internal piston. The macrostate of such a system is completely characterized by the extensive parameters of each of the simple systems; $U^{(1)}, V^{(1)}, N_1^{(1)} \dots N_r^{(1)}$ and $U^{(2)}, V^{(2)}, N_1^{(2)} \dots N_r^{(2)}$. However, for any given set of values of these variables there is an enormous number of ways in which the molecules of the system can be distributed at any instant. These different positions correspond to different microstates,