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*If you can't take the heat,  
Get out of the skillet.*

Because the beautiful and intricate subject of thermodynamics is covered by a number of good texts, it's understandable that astronomy books tend to bring in thermodynamic results on an ad hoc basis, as needed. Unfortunately, this often leads to a disjointed and confusing treatment. Let's recall some basic results of thermodynamics in a more systematic way.

### Macroscopic systems

The macroscopic quantities that characterize a thermodynamic system are called *state quantities*: they include internal energy  $U$ , volume  $V$ , entropy  $S$ , particle number  $N$  (in the case of a single type of particle), temperature  $T$ , pressure  $P$ , chemical potential  $\mu$ , and possibly other quantities such as applied magnetic or electric fields.

The quantities  $U$ ,  $V$ ,  $S$ , and  $N$  are *extensive* (global): if you subdivide a homogeneous part of the system in half, the value of any of these quantities splits equally between the halves. On the other hand,  $T$ ,  $P$ , and  $\mu$  are *intensive* (local): they have the same values in either half.

### First and second laws of thermodynamics

The first law of thermodynamics, applied to any infinitesimal process, states that

$$\delta U = \delta Q - \delta W$$

where the work done *by* the system is  $\delta W = P dV - \mu dN$  and the heat  $\delta Q$  absorbed by the system is *defined* by this relationship. The infinitesimal quantities  $\delta W$  and  $\delta Q$  are not exact differentials because work and heat are not state functions: the work done by the system in going between two states depends on how the transition is made, and similarly for the heat absorbed by the system.

The second law of thermodynamics states that, for a quasi-static (reversible) infinitesimal process, there exist macroscopic parameters  $S$  (entropy) and  $T$  (absolute temperature) such that

$$\delta Q = T dS$$

### Fundamental relationship for internal energy

Combining the above statements of the first and second laws gives a fundamental relationship of thermodynamics,

$$dU = T dS - P dV + \mu dN$$

This relationship describes the change in internal energy of the system when the extensive quantities  $S$ ,  $V$ , and  $N$  change under the influence of the intensive quantities  $T$ ,  $P$ , and  $\mu$ . The internal energy is called a *thermodynamic potential* because, if we know it as a *state function* of the other extensive variables,  $U = U(S, V, N)$ , we can derive complete knowledge of the macroscopic system—namely, the intensive quantities are obtained as derivatives of the fundamental relationship with respect to the extensive variables:

$$T = \left( \frac{\partial U}{\partial S} \right)_{V, N} \quad \text{and} \quad P = - \left( \frac{\partial U}{\partial V} \right)_{S, N} \quad \text{and} \quad \mu = \left( \frac{\partial U}{\partial N} \right)_{S, V}$$

These derivative equations are known as *equations of state*. So, for example, the middle equation above yields  $PV = NkT$  for an ideal gas. Note that, unlike a state function such as  $U(S, V, N)$ , a single equation of state like  $P(T, V, N)$  does not carry complete information about the system. If we know *all* the independent equations of state, we can recover the state function by integration.

We say “independent equations of state” because not all the intensive variables are independent. This can be understood in the following way. The ratio of two extensive variables is intensive. Only two independent intensive variables can be constructed from the three extensive variables  $S$ ,  $V$ , and  $N$ —e.g.,  $S/V$  and  $N/V$ . Any other intensive ratio (such as  $S/N$ ) can be derived from these two ratios.

We can derive a useful relationship by formalizing this reasoning. All the quantities in the state function  $U(S,V,N)$  are extensive. So, if we change (say, increase) the volume from  $V$  to  $\alpha V$ ,  $S$  becomes  $\alpha S$ ,  $N$  becomes  $\alpha N$ , and  $U$  becomes  $\alpha U$ . That is,

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

This contrasts with the behavior of an intensive variable such as temperature, for which

$$T(\alpha S, \alpha V, \alpha N) = T(S, V, N)$$

Now let  $\alpha$  be an infinitesimal increase,  $\alpha = 1 + \epsilon$ , and Taylor-expand  $U$ :

$$\begin{aligned} U(S + \epsilon S, V + \epsilon V, N + \epsilon N) &= U(S, V, N) + \epsilon S \left( \frac{\partial U}{\partial S} \right)_{V,N} + \epsilon V \left( \frac{\partial U}{\partial V} \right)_{S,N} + \epsilon N \left( \frac{\partial U}{\partial N} \right)_{S,V} \\ &= U + \epsilon U \end{aligned}$$

which requires by inspection that

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

Now substitute for the partial derivatives from the equations of state above to find

$$U(S, V, N) = TS - PV + N\mu$$

which is sometimes called Euler's equation. The total differential of Euler's equation is just

$$dU = T dS + S dT - P dV - V dP + N d\mu + \mu dN$$

which, when compared with the fundamental relationship  $dU = T dS - P dV + \mu dN$ , requires

$$S dT - V dP + N d\mu = 0$$

and shows explicitly how only two of the three intensive variables  $T$ ,  $P$ , and  $\mu$  can be chosen independently (this is known as the *Gibbs-Duhem relation*). By the same token, only two of the three equations of state are independent.

## Other thermodynamic potentials

Although the state function  $U(S,V,N)$  basically “says it all,” the state variables  $S$ ,  $V$ , and  $N$  are not always the most convenient. In many laboratory settings, it is easier to control an intensive variable such as  $T$  or  $P$ . In the context of stars, we may want to work with particular variables because they appear, for example, in the stellar structure equations. Are there other state functions—for example, a state function depending on  $T$ ,  $P$ , and  $N$ ? Remember, not just any function of these variables will preserve complete information about the system and thereby qualify as a state function.

It is shown in thermodynamics texts that three other thermodynamic potentials can be derived from  $U(S,V,N)$  by Legendre transformations. To each thermodynamic potential there corresponds a fundamental relationship analogous to  $dU = T dS - P dV + \mu dN$ .

It would take us too far afield to derive all the transformations, but we want to collect them (generalized to more than one species of particle) and show you a mnemonic device for remembering all the thermodynamic relationships when the particle numbers do not vary.

The thermodynamic potentials and their natural independent variables are

<b>Internal energy</b>	$U(S,V,N) = TS - PV + \sum \mu_i N_i$ $dU = T dS - P dV + \sum \mu_i dN_i$
<b>Enthalpy</b>	$H(S,P,N) = U + PV = TS + \sum \mu_i N_i$ $dH = T dS + V dP + \sum \mu_i dN_i$
<b>Helmholtz free energy</b>	$F(T,V,N) = U - TS = -PV + \sum \mu_i N_i$ $dF = -S dT - P dV + \sum \mu_i dN_i$
<b>Gibbs free energy</b>	$G(T,P,N) = U - TS + PV = \sum \mu_i N_i$ $dG = -S dT + V dP + \sum \mu_i dN_i$
<b>Gibbs-Duhem</b>	$0 = S dT - V dP + \sum N_i d\mu_i$

Equations of state can be read off from the fundamental relationships just as illustrated above for internal energy. For example, in the case of the Gibbs free energy,

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \quad \text{and} \quad V = -\left(\frac{\partial G}{\partial P}\right)_{T,N} \quad \text{and} \quad \mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j}$$

where the notation  $\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j}$  signifies the derivative with all variables except  $N_i$

kept constant. Note that, when there is only one species of particle,  $G = \mu N$  and the Gibbs free energy per particle is identical with the chemical potential.

### Maxwell relations

Returning to our old friends, the equations of state for  $U(S,V,N)$ ,

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \quad \text{and} \quad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \quad \text{and} \quad \mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_j}$$

we notice that we can exploit the fact that the second derivatives of  $U$  must be independent of the order in which the derivatives are taken. For example,

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

from which it follows that

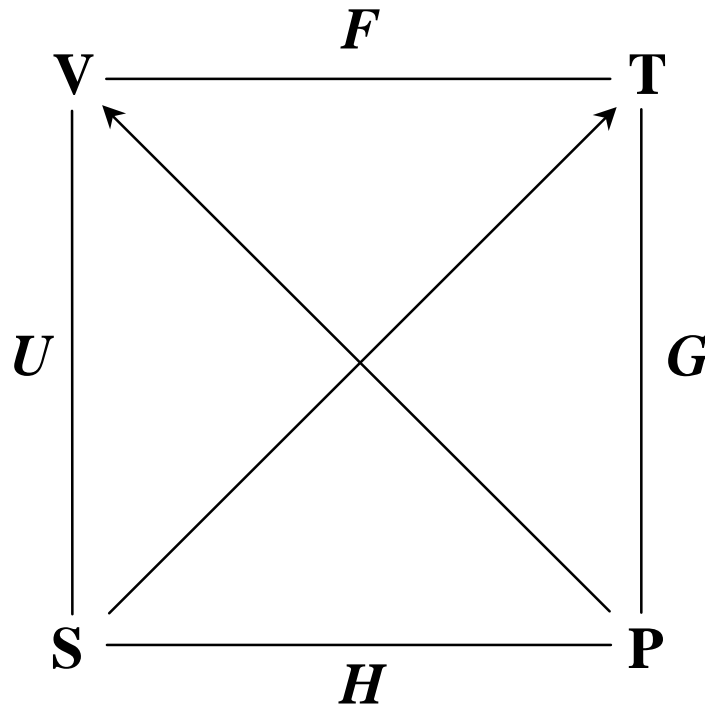
$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$$

Another example, involving a particle species, would be

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

These cross-derivative relations are called *Maxwell relations*. It's evident that we can derive a bewildering number of them. How can we call to mind a particular relation when we want it?

### The thermodynamic square



The mnemonic for drawing the square is: “To Verify Fundamental Thermodynamics, Get Powerful Help From Square’s Extremities.” The “To” reminds you first to draw an arrow *toward* a corner of the square. Then, start labeling from that corner around the square using the first letter of each word (“V”, “F”, “T”, “G”, “P”, “H”) until you hit “From,” at which point you draw an arrow *away from* the next corner. Then fill in the last two quantities from the first letters of the last two words, “S” and “E”. The only catch is that we are using “U” instead of “E” for the internal energy. You can use E as long as you remember what it is.

Now that we’ve drawn the square, what use is it?

1. The thermodynamic potentials  $U$ ,  $F$ ,  $G$ , and  $H$  are along the edges.

- Each potential is flanked by its natural variables; for example,  $H$  is flanked by  $S$  and  $P$ .
- You can extract the fundamental relationship for each potential from the corners opposite the natural variables. To continue with the  $H$  example: since  $H = H(S,P)$ , the fundamental relationship will have the form  $dH = \_\_\_ dS + \_\_\_ dP$ . Since  $T$  is opposite  $S$  and the arrow is pointing *toward*  $T$ , fill in  $T$  before  $dS$ ; likewise for  $V$  in front of  $dP$ . The result is  $dH = T dS + V dP$ .

As a second example, the square indicates that  $dG = \_\_\_ dT + \_\_\_ dP$ .  $S$  is opposite  $T$  but the arrow is pointing away from  $S$ , so fill in  $-S$ .  $V$  is opposite  $P$  and the arrow is pointing toward  $P$ , so fill in  $V$ . The result is  $dG = -S dT + V dP$ .

- You can read off the equations of state for each potential. For example, the derivative of  $F$  with respect to  $V$  is given by the variable diagonally across from  $V$ , with a negative sign because the arrow is pointing away from that variable—i.e.,  $(\partial F/\partial V)_T = -P$ . As another example,  $(\partial H/\partial S)_P = T$ .
- Finally, you can extract any of the Maxwell relations by matching pairs of variables in adjacent corners with their counterparts on the opposite side of the square. For example,  $S$  and  $P$  will be matched with  $V$  and  $T$  in the sense that  $\partial S/\partial P$  will be equated with  $\partial V/\partial T$ .  $\partial S/\partial P$  will be taken at constant  $T$  because the arrow from  $S$  points toward  $T$ .  $\partial V/\partial T$  will be taken at constant  $P$  because  $P$  is opposite  $V$ , but a minus sign will be used because the arrow is pointing away from  $P$ . The result is  $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$ .

Now, ain't that cool? Well, it is to us geeks.