Some Tools of Thermodynamics

Some Miscellaneous Relationships

Recall that the combined first and second laws give the relationship

$$dU = TdS - pdV. \quad (1)$$

This implies that U is a function of S and V. Sometimes we call S and V the "natural variables" of U. Regarding $U = U(S,V)$ we can write

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV. \quad (2)$$

Comparing Equations 1 and 2 it is clear that

$$\left(\frac{\partial U}{\partial S}\right)_V = T, \quad (3a)$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -p. \quad (3b)$$

These two equations can be regarded as thermodynamic definitions of T and p.

Likewise, from the definition of enthalpy we wrote before that

$$dH = TdS + Vdp. \quad (4)$$

Equation 4 implies that enthalpy is a natural function of S and p. Regarding $H = H(S,p)$ we can write

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp. \quad (5)$$

From Equations 4 and 5 it is clear that

$$\left(\frac{\partial H}{\partial S}\right)_p = T, \quad (6a)$$

and

$$\left(\frac{\partial H}{\partial p}\right)_S = V. \quad (6b)$$

Equations 6a and 6b give us another thermodynamic definition of T and a thermodynamic definition of V (which is curious since we have always regarded V as a purely mechanical variable).

Helmholtz and Gibbs Free Energy

When we made the transformation from U to H by the Legendre transformation,

$$H = U + pV, \quad (7)$$

we remarked that V was not the most convenient independent variable. In the laboratory it is usually much easier to control pressure than it is to control V. Since both U and H are natural functions of entropy, it is fair to ask how convenient it is to have S as a variable. The answer is that it is not at all convenient to control entropy or to have entropy as an independent variable. We do not have a meter that reads entropy and we do not know how to hold entropy constant as we change some other variable. (Recall that we can control temperature, pressure, and volume.) So we make some more Legendre transformations.

(We will not give an extensive discussion of Legendre transformations here, but we should point out that they are not arbitrary. You can't just pick any two variables you wish and put them together to make a Legendre transformation. We could make the Legendre transformation from U to H by adding the pV term to U only because V is related to p and U through Equation 3b. Using this as a guide it would seem reasonable to use Equation 3a to change the variable S to T in the function U, and use Equation 6a to change the variable S to T in the function H. Let's try it.)

Define the Helmholtz free energy, A, as

$$A \equiv U - TS. \quad (8)$$

Then,

$$dA = dU - TdS - SdT$$
$$= TdS - pdV - TdS - SdT$$
$$= -SdT - pdV. \quad (9a, b, c)$$

Equation 9c tells us that the Helmholtz free energy is a natural function of T and V. That is, $A = A(T,V)$. T and V are much more convenient variables than S and V. Regarding $A = A(T,V)$ we see that

$$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV. \quad (10)$$

Now compare Equation 10 with Equation 9c to see that,

$$\left(\frac{\partial A}{\partial T}\right)_V = -S, \quad (11a)$$

and

$$\left(\frac{\partial A}{\partial V}\right)_T = -p. \quad (11b)$$

Equation 11a gives us a thermodynamic definition of entropy and 11b gives another thermodynamic definition of pressure.

We now have a function of T and V, but we didn't much like V as an independent variable before so why should we like it any better now? Let's use the relationship 6a to define the Gibbs free energy, G, as,

$$G \equiv H - TS. \quad (12)$$

Actually, we can use any one of the three equivalent definitions,

$$G = H - TS$$
$$G = A + pV$$
$$G = U + pV - TS. \quad (13a, b, c)$$

Any one of Equations 13a, b, or c will give us the correct natural variables of G. Use Equation 12.

$$dG = dH - TdS - SdT$$
$$= TdS + Vdp - TdS - SdT$$
$$= -SdT + Vdp. \quad (14a, c, c)$$

From Equation 14c we see that the natural variables of G are temperature and pressure. Write

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp. \quad (15)$$

Comparing Equation 15 with Equation 14c we find that.

$$\left(\frac{\partial G}{\partial T}\right)_p = -S, \quad (16a)$$

and

$$\left(\frac{\partial G}{\partial p}\right)_T = V. \quad (16b)$$

Equation 16a gives us another thermodynamic definition of entropy and 16b another definition of volume.

Meaning of A and G

What do A and G mean and what are they good for? We said after the introduction of the first law (which introduced the internal energy, U) that we would be introducing three more functions that have units of energy. We now know that these functions are H, A, and G. At the time we said that only U has a simple physical meaning – the sum of all the kinetic and potential energies of all the particles. There is no simple physical explanation for enthalpy and the two free energies. The best we can do is tell how they are used.

1) Most simple-minded.

Set

$$dU = TdS - pdV + dw_{other}. \quad (17)$$

Then, using the definition of Helmholtz free energy as we have done above we find that,

$$dA = -SdT - pdV + dw_{other}. \quad (18)$$

For any process at constant temperature we have,

$$dA_T = -pdV + dw_{other} = dw_{all, reversib}. \quad (19)$$

That is, for a constant temperature process the Helmholtz free energy gives all the reversible work. For this reason the Helmholtz free energy is sometimes called the "work function." When a physicist says "free energy" without indicating Helmholtz or Gibbs, he usually means Helmholtz free energy.

Similarly, we can write,

$$dG = -SdT + Vdp + dw_{other}. \quad (20)$$

For a process at constant temperature *and* pressure we get,

$$dG_{T,p} = dw_{other} = dw_{all, non-pV}. \quad (21)$$

That is, for a process at constant temperature and pressure the change in Gibbs free energy gives all the reversible work except the pV work. This work might include electrical work, work creating surface area, and so on. Chemists do most of their reactions on the bench top at constant pressure. When a

chemist says "free energy" she almost always means Gibbs free energy unless she specifically states otherwise.

2) More useful - two new criteria for equilibrium

Recall that the second law of thermodynamics,

$$dS \geq \frac{dq}{T}, \quad (22)$$

gives us the fundamental criterion for equilibrium. That is, in a closed isolated system entropy seeks a maximum,

$$dS_{U,V} \geq 0 \quad (23)$$

Although this is the fundamental definition of equilibrium it is not the most useful definition because we do not often work with closed isolated systems. More often we work with systems at constant temperature and either constant volume or constant pressure. We can use the second law, Equation 22, and our new functions A and G to find criteria for equilibrium under these conditions.

Rewrite the second law, Equation 22 as follows:

$$TdS \geq dq$$
$$0 \geq dq - TdS, \quad (24)$$

or

$$dq - TdS \leq 0. \quad (25)$$

Now, going back to the original form of the first law with only pV work,

$$dU = dq - pdV, \quad (26)$$

and making the transformation to Helmholtz free energy we get,

$$dA = dU - TdS - SdT$$
$$= dq - pdV - TdS - SdT$$
$$= (dq - TdS) - pdV - SdT. \quad (27a, b, c)$$

For a process at constant temperature and volume we have,

$$dA_{T,V} = dq - TdS \leq 0. \quad (28)$$

We conclude that for a process at constant temperature and volume the Helmholtz free energy seeks a

minimum. Any spontaneous process in a system at constant T and V must decrease the Helmholtz free energy (if the system is away from equilibrium) or leave the Helmholtz free energy unchanged (if the system is at equilibrium).

By the same token, we can use the Gibbs free energy to discuss processes at constant temperature and pressure,

$$dG = dH - TdS - SdT$$
$$= dq + Vdp - TdS - SdT$$
$$= (dq - TdS) + Vdp - SdT, \quad (29a, b, c)$$

from which we conclude that for a process at constant T and p,

$$dG_{T,p} = dq - TdS \leq 0. \quad (30)$$

That is, at constant T and p the Gibbs free energy seeks a minimum. Any spontaneous process in a system at constant T and p must decrease the Gibbs free energy (if the system is away from equilibrium) or leave the Gibbs free energy unchanged (if the system is at equilibrium).

Maxwell's Equations

We now have the tools to derive some very useful relationships between thermodynamics variables. Maxwell's equations are based on the same principle as was Euler's test for exact differentials, namely that mixed second derivatives of "nice" functions must be equal. Applying this principle to our two new free energy functions we find,

$$\frac{\partial^2 A}{\partial V \partial T} = \frac{\partial^2 A}{\partial T \partial V}, \quad (31)$$

but we already know the first derivatives of A from Equations 11a and 11b. So,

$$\frac{\partial^2 A}{\partial V \partial T} = \frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)_V = \frac{\partial^2 A}{\partial T \partial V} = \frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T,$$

$$\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)_V = \frac{\partial}{\partial V}(-S) = \frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T = \frac{\partial}{\partial T}(-p),$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V. \quad (32a, b, c)$$

We obtain another similar equation from the Gibbs free energy.

Gibbs and Helmholtz Free Energies, Equilibrium, Maxwell's Relations

We now have four interesting and useful derivatives of entropy,

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \qquad \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p.$$

There are two other derivatives of entropy which might prove useful,

$$\left(\frac{\partial S}{\partial p}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial p}\right)_V$$

$$= \left(\frac{C_V}{T}\right)\left(\frac{\partial T}{\partial p}\right)_V. \qquad (37)$$

The other derivative, $\left(\dfrac{\partial S}{\partial V}\right)_p$, will be left to the reader.

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$$\frac{\partial^2 G}{\partial p \partial T} = \frac{\partial^2 G}{\partial T \partial p}, \qquad (33)$$

which becomes, using Equations 16a and 16b,

$$\frac{\partial^2 G}{\partial p \partial T} = \frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right)_p, \qquad \frac{\partial^2 G}{\partial T \partial p} = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right)_T,$$

$$\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right)_p = \frac{\partial}{\partial p}(-S) = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right)_T = \frac{\partial}{\partial T}(+V),$$

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p. \qquad (34a, b, c)$$

There are two more Maxwell's equations from dU and dH, but these are not as useful as the ones just derived. We will leave it to the reader to find the Maxwell's equations from dU and dH.

First Application of a Maxwell's Equation

As our first application of a Maxwell's equation we will derive the so-called thermodynamic equation of state which we stated without proof earlier. Write the combined first and second laws,

$$dU = TdS - pdV. \qquad (1)$$

Divide Equation 1 by dV and hold T constant to get,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p. \qquad (35)$$

Using the Maxwell's Equation, Equation 32c, to substitute for the entropy derivative we obtain,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p. \qquad (36)$$

Equation 36 is the equation that was written down without proof at the time we were discussing the Joule expansion.

The other version of thermodynamic equation of state, based on H instead of U, will be left as an exercise for the reader.

Summary