Affinity, Work, and Heat

Introduction[1]

The fundamental equation of thermodynamics comes in two forms. First, after defining entropy and limiting the number of ways that a system can exchange energy with its environment to two—heat and only one form of work (pressure-volume work), the fundamental equation is derived as

$$d\mathbf{U} = T\,d\mathbf{S} - P\,d\mathbf{V} \qquad [4.8]$$

If there is another way of changing the energy of a system, in addition to heat and pressure-volume work, another term must appear on the right side to preserve the equality. In the text, the emphasis is on chemical reactions, so this additional term is called "chemical work", and the fundamental equation becomes

$$d\mathbf{U} = T\,d\mathbf{S} - P\,d\mathbf{V} - \mathscr{A}\,d\xi \qquad [4.14]$$

where $\mathscr{A}$ is the Affinity and ξ is the progress variable. So equation [4.8] is simply a special case of equation [4.14]. It results when $\mathscr{A}\,d\xi$ is zero, i.e., there is no energy to be accounted for other than heat and the normal PV work done by the expansion or contraction of the system. A more general form of [4.8] is therefore

$$d\mathbf{U} \leq T\,d\mathbf{S} - P\,d\mathbf{V} \qquad [4.19]$$

which includes the possibility that energy in addition to $T\,d\mathbf{S}$ and $P\,d\mathbf{V}$ might exist, and we call this "extra" or "useful" energy, which could be used, for example, to lift a weight. The reason for the $<$ is this extra energy term, not the fact that $q < T\Delta S$ for irreversible processes, as is often stated. These fundamental equations an also be written in other energy forms, such as the Gibbs energy,

$$d\mathbf{G} = -\mathbf{S}\,dT + \mathbf{V}\,dP \qquad (1)$$
$$d\mathbf{G} = -\mathbf{S}\,dT + \mathbf{V}\,dP - \mathscr{A}\,d\xi \qquad [4.46]$$
$$d\mathbf{G} \leq -\mathbf{S}\,dT + \mathbf{V}\,dP, \qquad (2)$$

and from [4.46] we get

$$d\mathbf{G}_{T,P} = -\mathscr{A}\,d\xi \qquad [18.59]$$

The term "chemical work" for $\mathscr{A}\,d\xi$ is meant to suggest that it refers to work that could be done by a chemical reaction. Equation [18.59] was illustrated in a different way in § 4.13.1 by showing that that the change in Gibbs energy is a measure of the maximum amount of useful or extra work that can be obtained from a chemical reaction. But chemical reactions can also release/absorb heat, and in fact Prigogine and Defay (1954) refer to $\mathscr{A}\,d\xi$ as "uncompensated heat". How are these concepts reconciled?

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[1]Equation numbers for equations which appear in the text are given square brackets.

The Affinity[2]

It is established in the text (Chapter 4) that the fundamental equation [4.8] is the equation for the tangent plane to the **USV** surface if the differential terms are of any arbitrary magnitude, but more importantly it is the equation for the **USV** surface itself. That means that integration of $T\,d\mathbf{S} - P\,d\mathbf{V}$ between any two points on a **USV** surface (such as A' and B in Figure 1) will give the difference in **U**, $\Delta\mathbf{U}$, between those two points. The path followed by the integration (not necessarily the path followed by the real system) is the line on the **USV** surface, a reversible process. If there is another surface representing another equilibrium state of the same system, such as shown in Figure 1a, equation [4.8] can also be used for this surface, but the functional relations between T and $\mathbf{S}$ and between P and $\mathbf{V}$ will be different, so the calculated $\Delta\mathbf{U}$ will be different. What is important is that the equation refers only to stable or metastable equilibrium surfaces, along which changes, either reversible or irreversible, are effected by changes in the first and/or second constraints, $\mathbf{S}$ and $\mathbf{V}$. The same discussion can be applied any version of the fundamental equation, such as equation (1), so at this point we change from discussing the **USV** surface to the $\mathbf{G}TP$ surface, because **G** is the potential we actually use.[3]

The Gibbsite Reaction

Chemical reactions, such as equation [2.2],

$$\text{Al}_2\text{O}_3(s) + 3\,\text{H}_2\text{O}(l) = \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}(s) \qquad [2.2]$$
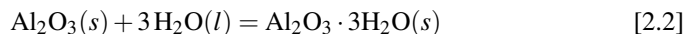
can be represented by two $\mathbf{G}TP$ surfaces, one for the reactants (in this case a metastable equilibrium assemblage) and one for the products (a stable equilibrium phase) as shown in Figure 1b, as well as the energy difference between them, shown by the arrow $A \rightarrow A'$. The fundamental equation (1) can be applied to changes along to either surface, such as $A' \rightarrow B$, so the problem now is to incorporate the energy difference represented by $A \rightarrow A'$ into our equation, so that we can calculate the energy difference between any two points on different surfaces, such as A and B.

We have chosen a particularly simple system to consider. When the process (chemical reaction) involves only pure phases, as in reaction [2.2], the reactant and product $\mathbf{G}TP$ surfaces remain fixed, because no change takes place in the **G** of either surface during the reaction. All that happens is that the reactants gradually change into products, but this change in the amounts of the phases does not affect the position of the surfaces—none of the phases change composition. A reaction between dissolved species, during which the concentrations of the species change, *does* change the **G** values and hence the position of the two surfaces.

Reaction [2.2] releases energy as it proceeds, so it represents a third source of energy, in addition to $T\,d\mathbf{S}$ and $P\,d\mathbf{V}$—it represents "extra" energy. To calculate Gibbs

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[2]As explained in §18.4, we use the total forms **U** and **G** in the relationship between these quantities and $\mathscr{A}\,d\xi$ in order to maintain dimensional consistency. In other words, the relation $dU = T\,dS - P\,dV - \mathscr{A}\,d\xi$ is dimensionally incorrect, because ξ is in moles and $\mathscr{A}$ is in $\text{J}\,\text{mol}^{-1}$.

[3]Also see section 7 in the Additional_Materials file for a numerical example using equation [4.46].
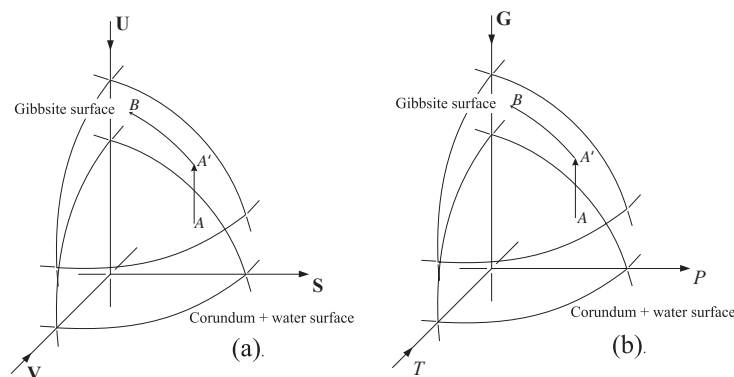
Figure 1: Modified from Figure 4.9 in the text by adding point *B*. (a). Surfaces representing two equilibrium states of the system Al_2O_3–H_2O in **USV** space, metastable corundum plus water, and stable gibbsite. The points *A, A′, B* are referred to in the text. (b). The same system in **G***TP* space. Note that **U** and **G** increase downwards.

energy differences between reactants and products, we must therefore add a third term to our fundamental equation (1). Looking at Figure 2 (Figure 4.8 in the text) for a clue as to how to do this, we see that we need to express this energy change as the slope (the change in **G** per increment of reaction, i.e., per number of moles reacted) multiplied by the the number of moles reacted. We call the change in **G** per mole of reaction the (negative) Affinity, $-\mathscr{A}$. The number of moles reacted is called ξ, which can vary from zero to any chosen number, but the range $0 \to 1$ is usually best. So the term we need is apparently $(\Delta\mathbf{G}/\Delta\xi)\cdot\xi$, or $-\mathscr{A}\cdot\xi$. In this simple case, this would in fact work, because as the two surfaces are fixed, $\Delta\mathbf{G}$ does not change during the reaction, and the slope $(\Delta\mathbf{G}/\Delta\xi)$ is a constant. So for one mole of reaction ($\xi = 1$) this expression gives $\Delta\mathbf{G}$, the total energy change for one mole of reaction, and at constant T,P this would in fact be represented by the arrow $A \to A'$.

Reactions Between Dissolved Substances

Reaction [2.2] does not normally reach an equilibrium state having all three phases. The reaction stops when one of the reactants is used up, but the activities of the products and reactants do not change during the reaction. In other cases the concentrations (activities) of the products and/or the reactants *do* change during the reaction, so as usual we must express the terms in our equation in derivative and differential form so as to be integrable. We must consider very small changes in ξ and the corresponding
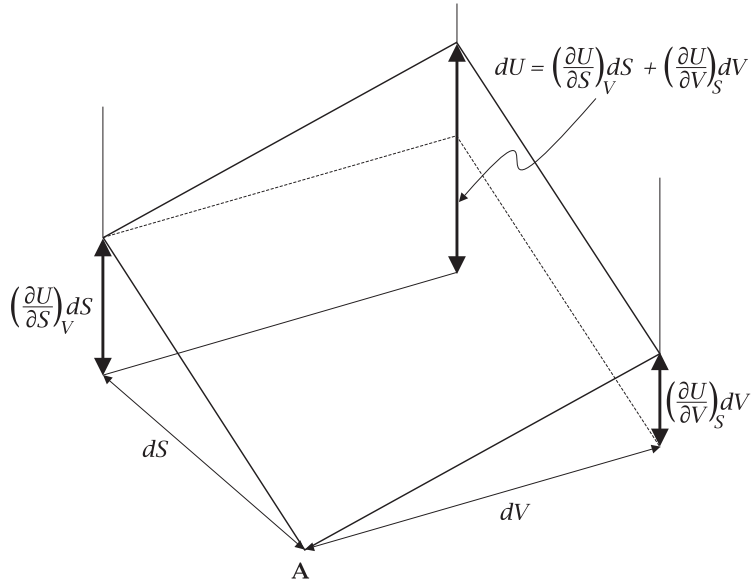
Figure 2: The tangent surface at a point A on a **USV** surface, showing how dU is geometrically related to dS and dV.

small changes in **G**, so a better definition of the Affinity is

$$-\mathscr{A} = \left(\frac{d\mathbf{G}}{d\xi} \right)_{T,P} \quad \text{or}$$

$$d\mathbf{G}_{T,P} = -\mathscr{A}\,d\xi \qquad [18.59]$$

Integration then gives

$$\Delta\mathbf{G}_{T,P} = -\int_{\xi=0}^{\xi=1} \mathscr{A}\,d\xi \qquad (3)$$

$$= \text{the energy change along the path } A \to A' \text{ in Figure 1.}$$

The Affinity is the rate of change of **G** with reaction progress, and as shown in Chapter 18, the *magnitude* of this rate of change is

$$\mathscr{A} = -\sum_{i}^{s} \nu_i \mu_i \qquad [18.57]$$

This means that after each increment of reaction the Affinity or rate of change is equal to the difference in Gibbs energy between the products and reactants, and therefore becomes zero when the reaction achieves equilibrium. This makes sense intuitively, because the rate at which the reaction proceeds towards equilibrium (the Affinity) should depend on how big the energy difference is between the reactants and products is, and will become zero at equilibrium. The rate of change towards the equilibrium state

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we are talking about has nothing to do with the real time kinetics of the reaction. It has rather to do with the magnitude of the change in reactants and products at each increment of ξ.

The Third Constraint

Also note in what sense ξ is our third constraint. When $\xi = 0$, we are at point A, a metastable state, held there by some third constraint, and when $\xi = 1$ we have arrived at point A', the corresponding stable equilibrium sate. In between, increments of ξ move us from A towards A', so that ξ is in fact the constraint, and "releasing the constraint" means allowing ξ to move in (irreversible) increments from 0 to 1. This is of course a fairly mathematical concept, and shows again why we insist on the difference between our thermodynamic models and the reality they are meant to simulate.

Physical Significance of the Affinity

We can generalize the arrow $A \rightarrow A'$ in Figure 1 to the energy difference between reactants and products of any reaction. This difference is the integral of the Affinity term $\int_{\xi=0}^{\xi=1} \mathscr{A} d\xi$, as shown in equation (3).

The next question is, what kind of energy is represented by this Affinity term? Obviously it is Gibbs energy, but changes in Gibbs energy are effected by transfers of work and/or heat, our only two kinds of energy transfer. As mentioned above, $\Delta \mathbf{G}$ can also be shown to be the maximum amount of extra work available from a process, in our case a chemical reaction. But chemical reactions in nature, such as metamorphic reactions deep in the crust, generally do not do any extra work.

The Two Kinds of Work

To investigate this further, we first look at an example of a chemical reaction doing extra work, as well as normal volume change work. To do this we use reaction [18.54] from Chapter 18,

$$N_2(g) + 3H_2(g) = 2NH_3(g) \qquad [18.54]$$
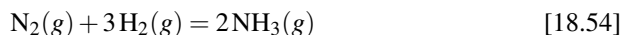
We are accustomed to using heat (enthalpy) and entropy data for such reactions, but how can this reaction produce work, that is, work *in addition to* the work that must be done because we are expanding (in the reverse direction) from 2 moles of gas to 4 moles against some confining pressure?

As mentioned above, the extra work obtainable from any thermodynamic process is either equal to or less than the change in Gibbs energy for that process. The maximum extra work is thus equal to the change in Gibbs energy, and this can only be obtained if the process or reaction is carried out reversibly. The example demonstrating this in the text (Chapter 3) is the expansion of a gas from an initial pressure to a lower pressure, where maximum work is only obtained with a reversible expansion. In the example the
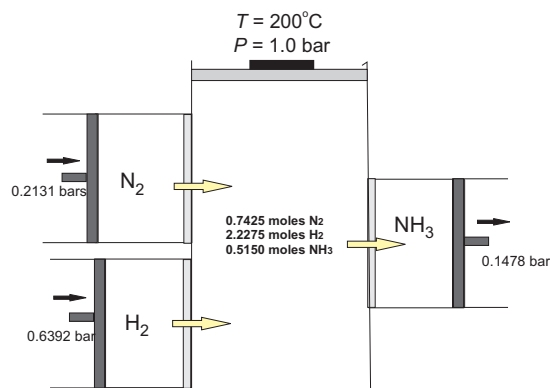
Figure 3: A Van't Hoff equilibrium box. 3 moles of H_2 and one mole of N_2 are pushed slowly into the reaction chamber at their equilibrium pressures, as 2 moles of NH_3 are simultaneously pulled slowly out, also at its equilibrium pressure. The reaction thus takes place at equilibrium, a reversible process. The box is enclosed in a thermostat which keeps the temperature constant at 200°C.

| T | P | $\log K$ | ΔG° | ΔH° | ΔS° |
°C	bar		$\mathrm{cal\,mol^{-1}}$	$\mathrm{cal\,mol^{-1}}$	$\mathrm{cal\,mol^{-1}\,K^{-1}}$
200	1.0	-0.406	879	-23702	-51.9

Table 1: Data for reaction [18.54] from SUPCRT92.

work done is not extra work but the normal work of expansion of the system. Nevertheless, the relation between maximum work and reversibility is perfectly general, and includes chemical reactions.

Data for reaction [18.54] from SUPCRT92 are shown in Table 1. The value of ΔG° (or $\Delta_r G^\circ$) at 200°C is positive, meaning that the reaction is spontaneous (irreversible) in the opposite direction to that written. In this opposite direction, two moles of reactant (NH_3) become four moles of product gases (N_2 and $3\,H_2$), and $\Delta_r G^\circ = -879\,\mathrm{cal\,mol^{-1}}$. The volume per mole of ideal gas is $22414\,\mathrm{cm^3}$ at 1.01325 bar and 273.15 K (Appendix A), or $39340\,\mathrm{cm^3}$ at 473.15 K and 1.0 bar, or $940.2\,\mathrm{cal\,bar^{-1}\,mol^{-1}}$, and so the work of expansion against the constant confining pressure of 1 bar is

$$w = -P\Delta V \tag{3.2}$$
$$= -1.0 \times 2 \times 940.2$$
$$= -2RT$$
$$= -2 \times 1.987 \times 473.15 \tag{4}$$
$$= -1880\,\mathrm{cal\,mol^{-1}} \tag{5}$$

negative, because the system is doing work.[4]

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[4] In the discussion of reaction [18.54] the term "per mole", as in $\mathrm{J\,mol^{-1}}$, $\mathrm{cal\,mol^{-1}}$, etc., refers to per mole of N_2, because N_2 has a stoichiometric coefficient of 1.0. This is discussed on p. 29 of the text.

In some reactions this $P\Delta V$ term is physically realizable, but in this case it is not. The ΔV term is just the difference in volumes of the pure phases, but realistically, if NH_3 reacts irreversibly it does not form pure N_2 and pure H_2. It forms a mixture of gases, and only until the equilibrium mixture is achieved, at which point the forward and reverse reactions become balanced, and the reaction effectively stops. The actual ΔV is the difference between the molar volume of the pure NH_3 starting composition and the molar volume of the equilibrium composition. Here again we see a difference between what happens in reality and what happens in the thermodynamic model. The theoretical $P\Delta V$ work of expansion shown in (5), as well as the additional extra or useful work available only in a reversible process, can be seen by considering the reaction taking place in a Van't Hoff equilibrium box.

Van't Hoff Equilibrium Box[5]

As shown in Figure 3, for the reaction to proceed reversibly, we must first attach three piston-cylinders to semi-permeable membranes on the reaction chamber, which allows us to push the pure reactant(s) in and to allow the pure product(s) to leave the reaction chamber at their equilibrium pressures. Note that "the system" now refers to the reaction chamber *plus* the piston-cylinder arrangements.

We start with the reaction chamber having the gas mixture at equilibrium at 200°C, and reactant NH_3 gas in a cylinder in its pure state at 1 bar and 200°C, the state for which we have data (Table 2). We then change the pressure of reactant NH_3 reversibly from 1 bar to its equilibrium pressure in its own cylinder without allowing it to enter the reaction chamber. Then we push this reactant gas into the chamber at its equilibrium pressure and allow the two product gases out, also at their equilibrium pressures. No change of composition or volume of the gas in the reaction chamber occurs, because equilibrium is maintained. Then we reversibly compress each product gas from their equilibrium pressures back to 1 bar. The net reaction is therefore reactant gas at 1 bar $\rightarrow$ pure product gases at one bar, and is the (reverse of) reaction [2.2], for which the data in Table 2 are applicable.

The work done is of two types. In pushing ammonia gas into the reaction chamber, we do $P\Delta V$ work, where P is the equilibrium pressure P_{NH_3} and ΔV is the volume of a mole of ideal gas at 473.15 K and P_{NH_3}. Because $P_1V_1 = P_2V_2$ for ideal gas, the $P\Delta V$ work done is identical to what it would be if P was 1 bar, because although the pressure is greater, the volume change is proportionally smaller. The same reasoning applies to the product gases. They exit at their smaller equilibrium pressures, but occupy much greater volumes than they would at 1 bar. The net resulting work done is shown in equation (5).

In addition to this "normal" PV work, extra work is done in changing the pressures of the reactants and products of the reaction to and from 1 bar and their equilibrium pressures. If the reaction is spontaneous, this will be useful work, done by the system. If the reaction is not spontaneous, as is the case with reaction [18.54] as written, this work must be done on the system. Let's calculate this work for the case shown in

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[5]This subject is treated in some detail, though not entirely correctly, by Bazhin and Parmon (2007). Another (correct) treatment is Steiner (1948), but he does not consider the heat aspect.

T	$\log K_{[18.54]}$	n_{N_2}	n_{H_2}	n_{NH_3}	ξ
°C		mol	mol	mol	
200	-0.4061	0.7425	2.2275	0.5150	0.2575

Table 2: Species mole numbers for reaction [18.54] at 1 bar and 200°C from Table 18.4 in the text.

Figure 3.

The Equilibrium Pressures

First we must determine the equilibrium partial pressure of each gas. The equilibrium number of moles of each species in the system is shown in Table 2, and the mole fractions of each times the total pressure gives the equilibrium pressure of each species. The total moles of species in equilibrium in the box is

$$\Sigma n = 0.7425 + 2.2275 + 0.5150$$
$$= 3.485 \tag{6}$$

so, for example, the equilibrium partial pressure of N_2 is

$$P_{N_2} = \frac{0.7425}{\Sigma n} \times 1.0 \tag{7.3}$$
$$= 0.2131 \text{bar} \quad \text{(as shown in Figure 3.)}$$

The Reversible Work

The reversible work done in changing the pressure of reactant NH_3 gas from 1 bar (P_1) to 0.1478 bar (P_2) is, with $n = 2$

$$w = -nRT \ln \frac{P_2}{P_1}$$
$$= -2RT \ln \frac{0.1478}{1}$$

The work done in changing the pressure of product gas H_2 from 0.6392 bar (P_1) to 1 bar (P_2)is, with $n = 3$,

$$w = -nRT \ln \frac{P_2}{P_1}$$
$$= -3RT \ln \frac{1}{0.6392}$$

and similarly for N_2. This change of pressure on an ideal gas has no heat effect (equation [5.42] in the text), but does change the entropy and thus the Gibbs energy of the gases. The entropy effect is[6]

$$\Delta S = R \ln \frac{P_1}{P_2} \tag{5.41}$$

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[6]Equation [5.41] is corrected in the second printing of the text.

so the Gibbs energy change is

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ \qquad [6.17]$$

$$= 0 - T \cdot R \ln \frac{P_1}{P_2}$$

$$= RT \ln \frac{P_2}{P_1}$$

$$= w \qquad [4.57]$$

The total net work, in addition to the "normal" PV work done is then

$$w = -2RT \ln \frac{0.1478}{1} - 3RT \ln \frac{1}{0.6392} - RT \ln \frac{1}{0.2131}$$

$$= -1.9872 \times 473.15 \times \ln \left(\frac{0.1478^2}{0.6392^3 \times 0.2131} \right)$$

$$= -879 \, \text{cal} \, \text{mol}^{-1}$$

The $\frac{0.1478^2}{0.6392^3 \times 0.2131}$ term is of course identical to the equilibrium constant for the reaction, so by considering available work we have shown again that

$$\Delta_r G^\circ = -RT \ln K \qquad [9.11]$$

which gives this standard relationship a meaning in terms of work.

The change in Helmholtz energy is the total work done, so

$$\Delta A = -879 - 1880$$

$$= -2759 \, \text{cal} \, \text{mol}^{-1}$$

The Heat Transfer

Equation [6.17] shows that the Gibbs energy change is related to changes in enthalpy and entropy. From Table 1, $\Delta_r H^\circ = 23702 \, \text{cal} \, \text{mol}^{-1}$ and

$$473.15 \times \Delta_r S^\circ = 24556 \, \text{cal} \, \text{mol}^{-1}$$

for the spontaneous direction. The difference is

$$\Delta_r H^\circ - 473.15 \times \Delta_r S^\circ = -854 \, \text{cal} \, \text{mol}^{-1}$$

This should of course agree with the tabulated value of $\Delta_r G^\circ$ of $(-)879 \, \text{cal} \, \text{mol}^{-1}$, but such errors are not uncommon in thermodynamic data. Both $\Delta_r H^\circ$ and $T \Delta_r S^\circ$ are quantities of energy, but $T \Delta_r S^\circ$ is energy available as heat from or to the thermostat to balance the energy requirements of the reaction. In this case the imbalance, which is

$$\Delta_r G^\circ - \Delta_r H^\circ = -T \Delta_r S^\circ$$

is negative, so $-24556 \, \text{cal} \, \text{mol}^{-1}$ (using the $-854 \, \text{cal} \, \text{mol}^{-1}$ value for $\Delta_r G^\circ$) is transferred from the system to the thermostat. In other cases, the imbalance between $\Delta_r G^\circ$ and $\Delta_r H^\circ$ is positive, and heat is added to the system from the thermostat.

Irreversible Work

So $879\,\mathrm{cal\,mol^{-1}}$ is an upper limit to the extra work done by reaction [18.54], and so is in one sense the value of $\int_{\xi=0}^{\xi=1} \mathscr{A}\,d\xi$. It would be represented by an arrow $A \to A'$ in Figure 1 if the lower surface was $\mathbf{G}_{\mathrm{NH_3}}$ and the upper surface was $\mathbf{G}_{\mathrm{N_2}} + 3\mathbf{G}_{\mathrm{H_2}}$. But although it is an upper limit, this quantity of energy is entirely hypothetical, not only because it requires a reversible process to be realized, but also because the real, irreversible, process is entirely different. As mentioned above, the real process is not between reactants and products as pure gases, but between pure gases and an equilibrium mixture of gases. The two surfaces just mentioned, representing the pure gases, do not stay fixed as the reaction proceeds, but approach one another and become a single surface when the reaction reaches equilibrium.[7] The Affinity is not constant, as in reaction [2.2], but changes from a maximum value to zero, as shown in Figure (18.10) in the text.

Volume Change Work

The number of moles of gas in the reaction chamber at equilibrium is 3.485 (equation (6)), so the change in moles in the irreversible reaction is

$$\Delta n = 3.485 - 4$$
$$= -0.515 \quad \text{from } \mathrm{N_2 + 3H_2}$$

and

$$\Delta n = 3.485 - 2$$
$$= 1.485 \quad \text{from } \mathrm{2NH_3}$$

The resulting volume change is performed at a pressure of 1 bar, so the work done is

$$w = -P\Delta V$$
$$= -\Delta nRT$$
$$= 0.515 \times 1.987 \times 473.15$$
$$= 484\,\mathrm{cal\,mol^{-1}} \quad \text{from } \mathrm{N_2 + 3H_2} \text{ to equilibrium,}$$

or

$$w = -P\Delta V$$
$$= -\Delta nRT$$
$$= -1.485 \times 1.987 \times 473.15$$
$$= -1396\,\mathrm{cal\,mol^{-1}} \quad \text{from } \mathrm{2NH_3} \text{ to equilibrium.}$$

and of course
$$-484 - 1396 = -1880\,\mathrm{cal\,mol^{-1}}$$

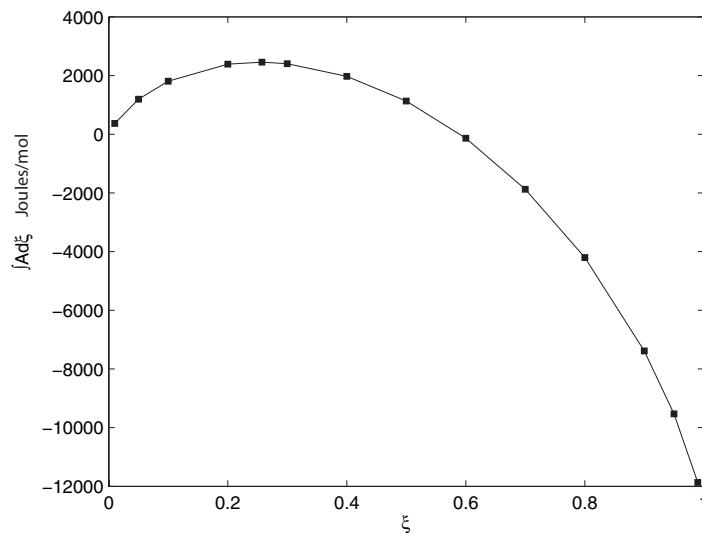[7]Here we imagine the pure gases as existing initially together in the reaction chamber, not in separate cylinders.

Figure 4: The value of $\int_{\xi=0}^{\xi=1} \mathscr{A} d\xi$

as before. So $484\,\mathrm{cal\,mol^{-1}}$ work energy is added to the system when N_2 and $3H_2$ react to equilibrium, and $-1396\,\mathrm{cal\,mol^{-1}}$ work energy is performed by the system when reacting from $2\,NH_3$ to equilibrium. This is the normal work done in a reaction due to the change in volume.

Extra Work

The maximum extra work from this reaction is $897\,\mathrm{cal\,mol^{-1}}$ using a highly hypothetical situation, but a more realistic estimate is given by the value of $\int_{\xi=1}^{\xi=0.2575} \mathscr{A} d\xi$, that is, the integrated value of the arrow $A \rightarrow A'$ as the reaction proceeds irreversibly from pure NH_3 to the equilibrium composition at $\xi = 0.2575$. One might imagine two moles of pure NH_3 pushed into the reaction chamber at 1 bar pressure, then reacting there to the equilibrium mixture.

This calculation was performed in MATLAB, by first differentiating equation [18.65] with respect to ξ, obtaining an expression for $d\mathbf{G}/d\xi$, then integrating $(d\mathbf{G}/d\xi)d\xi$.[8] The result is shown in Figure 4. The maximum value of $\int \mathscr{A} d\xi$ occurs at the equilibrium value of $\xi = 0.2575$, and is $2455\,\mathrm{J\,mol^{-1}}$, or $587\,\mathrm{cal\,mol^{-1}}$. This represents the extra work available from this irreversible reaction as it proceeds to equilibrium and is

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[8]The expression for this derivative is shown in the answer to question 3 in the Chapter 18 section of the Book_Problems on the CUP web site.

clearly less than the hypothetical maximum.

$$-\int_{1}^{0.2575} \mathscr{A}\,d\xi = \int_{0}^{0.2575} \mathscr{A}\,d\xi$$
$$= 587\,\mathrm{cal\,mol^{-1}}, \quad \text{and}$$
$$587 < 897$$

In this case the extra energy appears as volume change work, but in general it is simply a quantity of energy available from the system. If the system is arranged such that no extra work is performed, this energy would be available as heat. Gaseous systems such as this one are best suited to use the energy represented by the Affinity term as (additional) volume change work, but other reactions such as those in aqueous solution can be carried out in galvanic cells, and can use the extra energy in other ways.

Uncompensated Heat

Prigogine and Defay (1954, Chapter 3) introduce the term "uncompensated heat", which they attribute to De Donder (1920). This is a quantity of heat generated within a closed system due to an irreversible process such as a chemical reaction, and because they explicitly exclude all non-PV work (their equations (2.2) and (2.3)) it is one interpretation of $\int \mathscr{A}\,d\xi$. Thus they write

$$dQ' = \mathscr{A}\,d\xi \geq 0 \tag{3.21}$$

where Q' is the uncompensated heat. When Q' (or dQ') is zero, the system is at stable equilibrium.

Natural processes generally do no work other than PV work. For example, metamorphic reactions will generate or absorb heat (retrograde and prograde reactions respectively) and will do PV work as the rocks change volume, but despite being close to quasistatic, will do no other kinds of work. In these cases $\int \mathscr{A}\,d\xi$ represents the heat generated or absorbed. So if we are interested only in natural processes, then we should perhaps follow Prigogine and Defay and regard the term $\mathscr{A}\,d\xi$, the energy released in irreversible processes, as representing heat.

References

Bazhin, N.M., and Parmon, V.N., 2007, Conversion of chemical reaction energy into useful work in the Vant Hoff equilibrium box. Jour. Chemical Education, v. 84, pp. 1053–1055.

Denbigh, K., 1966, The Principles of Chemical Equilibrium: Cambridge, Cambridge University Press, 494 pp.

De Donder, Th. (with F.H. van den Dungen and G. van Lerberghe), 1920, Leçons de Thermodynamique et de Chimie-Physique. Gauthiers-Villars, Paris.

Prigogine, I., and Defay, R., 1954, Chemical Thermodynamics. London, Longmans Green, 543 pp.

Steiner, L.E., 1948, Introduction to Chemical Thermodynamics, 2nd edition, Mc-Graw Hill, New York.