THE DEPENDENCE OF FREE ENERGY UPON TEMPERATURE

BY J. E. TREVOR

Two relatively recent articles, one by Richards¹, the other in connection therewith by van't Hoff², deal with the thermodynamic theory of free energy. The interest aroused by these articles seems to render desirable a critical examination of the theoretical results that they record.

An integration by van't Hoff

When the thermodynamic state of a system is determined by 'normal variables', the difference of the specific heats of the system at two end-states having the same temperature is easily expressed by means of the free energy of the system. Van't Hoff's paper is primarily concerned with the integration of this relation with regard to the temperature, under the assumption that the difference of the specific heats is independent of the temperature.

Let us examine this operation from the beginning. When the state-variables of the system are the absolute temperature θ and the 'parameters'

$$x_1, x_2 \dots x_n,$$

the specific heat c_x at constant parameters is defined by the equation

$$\begin{aligned} c_x &= + \theta \frac{\partial \eta}{\partial \theta} \\ (1) \qquad &= - \theta \frac{\partial^2 f}{\partial \theta^2}, \end{aligned}$$

where η denotes the specific entropy, and f the specific free energy of the system. Considering two states characterized by different values of the parameters, and writing

$$\begin{aligned} \Delta c_x &= c_x(x_{12}, x_{22} \dots x_{n2}, \theta) - c_x(x_{11}, x_{21} \dots x_{n1}, \theta) \\ \Delta f &= f(x_{12}, x_{22} \dots x_{n2}, \theta) - f(x_{11}, x_{21} \dots x_{n1}, \theta), \end{aligned}$$

¹ Proc. Am. Acad. 38, 293; Zeit. phys. Chem. 42, 129 (1902).

² Boltzmann. Festschrift, 233 (1904).

we obtain from (1) the relation in question

$$(2) \quad \frac{\partial^2 \Delta f}{\partial \theta^2} = -\frac{\Delta c_x}{\theta}.$$

The quantity Δc_x in this familiar equation is a function of the specified end-values of the variables. Integration over a temperature interval $\theta - \theta_0$ such that within it Δc_x is sensibly independent of the temperature yields

$$(3) \quad \frac{\partial \Delta f}{\partial \theta} - \left(\frac{\partial \Delta f}{\partial \theta} \right)_0 = -\Delta c_x \cdot \log \theta + \Delta c_x \cdot \log \theta_0.$$

Integrating again, writing $-\Delta \eta_0$ for the negative change, $\partial \Delta f / \partial \theta$, of the specific entropy at θ_0 , we find

$$(4) \quad \Delta f - \Delta f_0 = (\Delta c_x - \Delta \eta_0)(\theta - \theta_0) - \Delta c_x \theta \cdot \log \frac{\theta}{\theta_0}.$$

This integration was executed by Helmholtz, in 1882, in his famous exposition of the free energy theory. In our notation, Helmholtz's equation (17), found by integrating (1) with regard to the temperature, is

$$f - f_0 = (c_x - \eta_0)(\theta - \theta_0) - c_x \theta \cdot \log \frac{\theta}{\theta_0}.$$

Writing this equation for two states at the same temperature, and subtracting, we obtain (4), the equation sought by van't Hoff.

If the equation (4) be written

$$(4a) \quad \begin{aligned} \Delta f = & -\Delta c_x \theta \cdot \log \theta \\ & + (\Delta c_x - \theta \eta_0 + \Delta c_x \log \theta_0) \cdot \theta \\ & - \Delta c_x \theta_0 + \Delta \eta_0 \theta_0 + \Delta f_0, \end{aligned}$$

and A be written for the coefficient of θ , and E_0 for the sum of the terms that do not contain θ , the equations (4a) and (3) become

$$\Delta f = E_0 + A\theta - \Delta c_x \theta \cdot \log \theta$$

$$\frac{\partial \Delta f}{\partial \theta} = A - \Delta c_x (1 + \log \theta).$$

These equations appear to be identical with the equations (4*b*) and (4*c*) obtained by van't Hoff,

$$E = E_0 + AT - ST \log T$$

$$\frac{dE}{dT} = A - S(1 + \log T).$$

(It will be noted that van't Hoff writes E for Δf , and Q for the corresponding isothermal difference of energy Δe .) Yet van't Hoff's equations, with the meanings that he attaches to their terms, are incorrect. The reason for this is that van't Hoff integrates from $\theta = 0$, thereby assuming Δc_x to be entirely independent of θ . This assumption is inadmissible. The correct formulation is that of equation (4), and is due to Helmholtz.

The hypothesis of Richards

In the paper by Richards, cited by van't Hoff, it is inquired whether isothermal change of the heat capacity of a thermodynamic system "has any causal relationship to the relative magnitudes of the free energy change and the heat of the reaction." In a brief abstract¹ of this paper, I observed that the relation between the change of the heat capacity (for constant 'normal' parameters) and the simultaneous change of the free energy is that expressed by (2) above,

$$\Delta c_x = -\theta \frac{\partial^2 \Delta f}{\partial \theta^2}.$$

Again, from certain experimental data, Richards draws the conclusion that "the change of the free energy with the temperature must have some fundamental connection with the change of the total energy with the temperature," and that this connection is

$$(5) \quad \frac{\partial \Delta f}{\partial \theta} = -M \frac{\partial \Delta e}{\partial \theta},$$

where M is independent of θ . I commented on this by pointing out that such a relation does exist, and that it has the familiar form

$$\frac{\partial \Delta e}{\partial \theta} = -\theta \frac{\partial^2 \Delta f}{\partial \theta^2}.$$

¹ This Journal, 7, 223 (1903).

It appears, however, if I correctly understand a letter from Prof. Richards on the matter, that the aim of the investigation in question was to establish, through appeal to experiment, an algebraic relation between the derivatives

$$\frac{\partial \Delta e}{\partial \theta} \text{ and } \frac{\partial \Delta f}{\partial \theta}.$$

From the principles of thermodynamics, such a relation cannot be obtained; it may be that none exists. Differentiation of

$$\Delta e = \Delta f + \theta \Delta \eta$$

yields a relation involving these two derivatives,

$$\frac{\partial \Delta e}{\partial \theta} = \frac{\partial \Delta f}{\partial \theta} + \frac{\partial(\theta \Delta \eta)}{\partial \theta};$$

and by combining this with (5), whereby we obtain

$$\frac{\partial \Delta f}{\partial \theta} = - \frac{M}{1 + M} \frac{\partial(\theta \Delta \eta)}{\partial \theta},$$

and integrating from a temperature of reference θ_0 , we find (5) to require

$$\Delta f - \Delta f_0 = - \frac{M}{1 + M} \theta \Delta \eta + \frac{M}{1 + M} \theta_0 \Delta \eta_0.$$

Now, in general we have

$$\Delta f - \Delta f_0 = \Delta e - \Delta e_0 - \theta \Delta \eta + \theta_0 \Delta \eta_0;$$

whereupon elimination of

$$\Delta f - \Delta f_0 + \theta \Delta \eta$$

between these two equation yields

$$(6) \quad \Delta e - \Delta e_0 = \frac{1}{1 + M} \theta \Delta \eta - \frac{1}{1 + M} \theta_0 \Delta \eta_0.$$

For $\Delta e - \Delta e_0$, we have

$$\Delta c_x = \theta \frac{\partial \Delta \eta}{\partial \theta} = \frac{\partial \Delta e}{\partial \theta}$$

$$\Delta e - \Delta e_0 = \int_{\theta_0}^{\theta} \Delta c_x d\theta;$$

and, for $\Delta\eta$,

$$\frac{\partial \Delta\eta}{\partial \theta} = \frac{\Delta c_x}{\theta}$$

$$\Delta\eta = \int_{\theta_0}^{\theta} \frac{\Delta c_x}{\theta} d\theta + \Delta\eta_0;$$

so, by substitution of these values, (6) becomes

$$\int_{\theta_0}^{\theta} \Delta c_x \left(\frac{1}{\theta_1} - \frac{1}{1+M} \frac{1}{\theta} \right) d\theta = -\theta_0 \frac{\Delta\eta_0}{1+M} \frac{1}{\theta} + \frac{\Delta\eta_0}{1+M},$$

where θ_1 signifies the (constant) upper limit of the integral.

The assumption of (5) is, thus, equivalent to the hypothesis that the relation between Δc_x and θ is of the form

$$\int_{\theta_0}^{\theta} \Delta c_x \left(\frac{1}{\theta_1} - \frac{1}{1+M} \frac{1}{\theta} \right) d\theta = a \left(1 - \frac{\theta_0}{\theta} \right),$$

where a is independent¹ of θ .

The meaning of the hypothesis of Richards

But the assumption proposed can be more simply expressed, it is equivalent to the hypothesis that isothermal changes of specific heat are proportional to the $1/M$ -th power of the temperature. This may be shown by combining the assumed relation (5),

$$\frac{\partial \Delta f}{\partial \theta} = -M \frac{\partial \Delta e}{\partial \theta},$$

with the general thermodynamic equation

$$-\theta \frac{\partial^2 \Delta f}{\partial \theta^2} = \frac{\partial \Delta e}{\partial \theta}.$$

Eliminating $\partial \Delta e / \partial \theta$ between these equations, we replace (5) by the formulation

$$\frac{\partial \Delta f}{\partial \theta} = M\theta \frac{\partial^2 \Delta f}{\partial \theta^2}.$$

¹ It is a function of the end values of the parameters.

This equation, in the form

$$\frac{\partial}{\partial \theta} \log \frac{\partial \Delta f}{\partial \theta} = \frac{\partial}{\partial \theta} \log \theta^{1/M},$$

can be integrated with regard to θ , whence

$$(7) \quad \frac{\partial \Delta f}{\partial \theta} = - \frac{\Delta \eta_0}{\theta_0^{1/M}} \theta^{1/M};$$

whence integrating again,

$$(8) \quad \begin{aligned} \Delta f = & - \frac{M}{1+M} \frac{\Delta \eta_0}{\theta_0^{1/M}} \theta^{1/M+1} \\ & + \frac{M}{1+M} \frac{\Delta \eta_0}{\theta_0^{1/M}} \theta_0^{1/M+1} + \Delta f_0. \end{aligned}$$

The isothermal change of specific heat satisfying the relation

$$\Delta c_x = \theta \frac{\partial \Delta \eta}{\partial \theta},$$

we have, by (7), since $-\Delta \eta = \partial \Delta f / \partial \theta$,

$$(9) \quad \Delta c_x = \frac{1}{M} \frac{\Delta \eta_0}{\theta_0^{1/M}} \theta^{1/M};$$

i. e., as asserted, Richards's assumption (5) is equivalent to the hypothesis that Δc_x is proportional to the $1/M$ -th power of the temperature.

Incidentally, it is not without interest to seek the form, as determined by (5), of the dependence of Δe on θ . By means of (7), the equation

$$\begin{aligned} \frac{\partial \Delta e}{\partial \theta} &= \theta \frac{\partial \Delta \eta}{\partial \theta} \\ &= \Delta c_x \end{aligned}$$

becomes

$$\frac{\partial \Delta e}{\partial \theta} = \frac{1}{M} \frac{\Delta \eta_0}{\theta_0^{1/M}} \theta^{1/M};$$

whence, integrating¹,

$$(10) \quad \Delta e = \frac{1}{1+M} \frac{\Delta \eta_0}{\theta_0^{1/M}} \theta^{1+1/M} \\ + \Delta e_0 - \frac{1}{1+M} \frac{\Delta \eta_0}{\theta_0^{1/M}} \theta_0^{1+1/M}.$$

Richards's assumption, then, as expressed by the equations (7), (9), (8), (10), may be stated in any one of the forms:

$$(7a) \quad \Delta \eta = a_1 \theta^{1/M}$$

$$(9a) \quad \Delta c_x = \frac{a_1}{M} \theta^{1/M}$$

$$(8a) \quad \Delta f = - \frac{M a_1}{1+M} \theta^{1+1/M} + a_2$$

$$(10a) \quad \Delta e = + \frac{a_1}{1+M} \theta^{1+1/M} + a_2;$$

where

$$a_1 = \frac{\Delta \eta_0}{\theta_0^{1/M}}, \quad a_2 = \Delta f_0 + \frac{M a_1}{1+M} \theta_0^{1+1/M},$$

and M , a_1 , a_2 , are independent² of θ .

¹ The sum of the additive terms in the equation (10) for Δe is equal to the sum of the additive terms in the equation (8) for Δf . For, when $\theta = 0$, we have $\Delta f = \Delta e$, and the equations (10) and (8) give

$$\Delta e_0 - \frac{a_1}{1+M} \theta_0^{1+1/M} = \Delta f_0 + \frac{M a_1}{1+M} \theta_0^{1+1/M},$$

which reduces to

$$\Delta e_0 = \Delta f_0 + a_1 \theta_0^{1+1/M},$$

which converts the sum of the additive terms in (10) to

$$\Delta f_0 + \frac{M a_1}{1+M} \theta_0^{1+1/M},$$

identical with the corresponding sum in (8).

² Here M is a constant, and a_1 , a_2 are functions of the end values of the parameters. As a check on these formulations, it may be noted that substitution for Δe and Δf from (10a) and (8a) in the general equation

$$\Delta e - \Delta f = \theta \Delta \eta$$

yields

$$a_1 \theta^{1+1/M} = \theta \Delta \eta,$$

which is identical with (7a).

The hypothesis (9a) may be stated in a more elementary way when it is converted into a statement concerning the form of the specific heat $c_x(x, \theta)$. Writing (9a)

$$c_{x2} - c_{x1} = \frac{\alpha_2 - \alpha_1}{M} \theta^{1/M},$$

it appears that Richards's hypothesis is tantamount to the assumption that the dependence of c_x on the temperature must satisfy the relation

$$(9b) \quad c_x = \frac{\alpha(x)}{M} \theta^{1/M} + \phi(\theta).$$

So Richards's proposal sifts down to a hypothesis concerning the forms of the specific heats of thermodynamic systems. He assumes that isothermal changes of specific heat are proportional to a constant (the $1/M$ -th) power of the temperature. Most thermodynamic questions of fundamental importance sift down to questions about the forms of specific heats. And here is where *measurements* are needed. A comprehensive experimental study of the heat capacity of some one system throughout the region of its accessible states would be of great interest and value.¹

Direct test of Richards's hypothesis

If, for any system, it should prove possible to make experimental determinations of Δc_x at different temperatures, these determinations could be employed to test the assumption of Richards as expressed² by the equation (9a),

$$\begin{aligned} \Delta c_x &= \frac{a_1}{M} \theta^{1/M} \\ &= A \theta^{1/M}. \end{aligned}$$

¹ I learn from Professor Richards that such a study of more than one special case is now in progress at the Chemical Laboratory of Harvard College, under his direction.

² Professor Richards requests me to state that he "made no definite assertion concerning the constancy of M , but intended merely to suggest that the two coefficients were perhaps mutually functions of one another, with opposite signs." The statement in his paper is: "The free energy of a given reaction changes on the average about twice as fast as the total energy with change of temperature, but in the opposite direction. When the total energy increases, the free energy diminishes. Expressed algebraically, $(\partial A/\partial T) = -M(\partial U/\partial T)$, in which the value of M averages about 2." It is this formulation that is here discussed.

At two temperatures, θ_1 and θ_2 , we should have two equations between the two unknowns A, M,

$$\begin{cases} (\Delta c_x)_1 = A\theta_1^{1/M} \\ (\Delta c_x)_2 = A\theta_2^{1/M}. \end{cases}$$

Eliminating A between these equations, we find

$$M = \frac{\log \theta_2 - \log \theta_1}{\log \Delta_2 - \log \Delta_1},$$

writing Δ_i for $(\Delta c_x)_i$. This is the equation for the determination of M from experiment. Eliminating M, we find

$$\log A = \frac{\log \theta_1 \log \Delta_2 - \log \theta_2 \log \Delta_1}{\log \theta_1 - \log \theta_2},$$

which is the equation for determining A from experiment.

It may be added that, if A, M be really constant throughout a region including the temperatures θ_1 , θ_2 , θ_3 , we should find identically verified the relation obtained by eliminating A, M between *three* equations¹,

$$\begin{vmatrix} \log \frac{\theta_1}{\theta_2} & \log \frac{\theta_1}{\theta_3} \\ \log \frac{\Delta_1}{\Delta_2} & \log \frac{\Delta_1}{\Delta_3} \end{vmatrix} = 0.$$

Condition for the existence of a relation $F = 0$

In this matter it would be of the greatest interest to prove or to disprove the existence of a relation

$$F\left(\frac{\partial \Delta e}{\partial \theta}, \frac{\partial \Delta f}{\partial \theta}\right) = 0.$$

When the state of the thermodynamic system is determined by two normal variables x, θ , the necessary and sufficient condition for the existence of this relation is

¹ The curiously symmetrical form of this relation is very apparent when it is written

$$\begin{pmatrix} \Delta_1 \\ \Delta_3 \end{pmatrix} \log \frac{\theta_1}{\theta_2} = \begin{pmatrix} \Delta_1 \\ \Delta_2 \end{pmatrix} \log \frac{\theta_1}{\theta_3}.$$

$$\begin{vmatrix} \frac{\partial^2 \Delta e}{\partial x \partial \theta} & \frac{\partial^2 \Delta e}{\partial \theta^2} \\ \frac{\partial^2 \Delta f}{\partial x \partial \theta} & \frac{\partial^2 \Delta f}{\partial \theta^2} \end{vmatrix} = 0.$$

Let us express the derivatives in this jacobian by means of derivatives of $\Delta\eta$. From

$$\begin{aligned} de &= Xdx + \theta d\eta \\ &= \left(X + \theta \frac{\partial \eta}{\partial x} \right) dx + \theta \frac{\partial \eta}{\partial \theta} d\theta, \end{aligned}$$

we find

$$\begin{cases} \frac{\partial \Delta e}{\partial \theta} = \theta \frac{\partial \Delta \eta}{\partial \theta} \\ \frac{\partial^2 \Delta e}{\partial x \partial \theta} = \theta \frac{\partial^2 \Delta \eta}{\partial x \partial \theta} \\ \frac{\partial^2 \Delta e}{\partial \theta^2} = \frac{\partial \Delta \eta}{\partial \theta} + \theta \frac{\partial^2 \Delta \eta}{\partial \theta^2}; \end{cases}$$

and we have

$$\begin{aligned} \frac{\partial^2 \Delta f}{\partial x \partial \theta} &= - \frac{\partial \Delta \eta}{\partial x} \\ \frac{\partial^2 \Delta f}{\partial \theta^2} &= - \frac{\partial \Delta \eta}{\partial \theta}. \end{aligned}$$

These values convert our jacobian to

$$- \theta \frac{\partial^2 \Delta \eta}{\partial x \partial \theta} \frac{\partial \Delta \eta}{\partial \theta} + \frac{\partial \Delta \eta}{\partial x} \frac{\partial \Delta \eta}{\partial \theta} + \theta \frac{\partial \Delta \eta}{\partial x} \frac{\partial^2 \Delta \eta}{\partial \theta^2} = 0,$$

which may be written

$$\frac{\partial}{\partial \theta} \log \frac{\frac{\partial \Delta \eta}{\partial x}}{\frac{\partial \Delta \eta}{\partial \theta}} = \frac{1}{\theta};$$

whence, integrating with regard to θ ,

$$\frac{\frac{\partial \Delta \eta}{\partial x}}{\frac{\partial \Delta \eta}{\partial \theta}} = \frac{1}{\theta_0} \frac{\left(\frac{\partial \Delta \eta}{\partial x} \right)}{\left(\frac{\partial \Delta \eta}{\partial \theta} \right)} \cdot \theta$$

$$(11) \quad = b\theta,$$

where b is a function of the end values of x . Making $x_2 - x_1 = dx$, and setting

$$\beta(x) = b(x, x + dx),$$

the equation (11) becomes

$$(12) \quad \frac{\partial^2 \eta}{\partial x^2} = \beta \theta \frac{\partial^2 \eta}{\partial x \partial \theta}.$$

This is, then, the necessary and sufficient condition for the existence of a relation $F = 0$. It requires that the specific heat of the system shall satisfy the equation

$$(12a) \quad \frac{\partial c_x}{\partial x} = \frac{1}{\beta} \frac{\partial^2 \eta}{\partial x^2}.$$

This condition, since

$$df = Xdx - \eta d\theta,$$

may be written in the equivalent form,

$$(12b) \quad \frac{\partial c_x}{\partial x} = - \frac{1}{\beta} \frac{\partial^2 X}{\partial x \partial \theta}.$$

It is not apparent that the principles of thermodynamics bear upon the possibility of the existence of this relation.

It is easily seen that the necessary and sufficient condition (11) is satisfied by Richards's formulation. This formulation has been shown to be equivalent to equations (7a) and (9a),

$$\Delta \eta = \Delta \alpha \cdot \theta^{1/M}$$

$$\Delta c_x = \frac{\Delta \alpha}{M} \theta^{1/M},$$

from the first of which follows

$$\frac{\partial \Delta \eta}{\partial x} = \frac{d\Delta \alpha}{dx} \theta^{1/M};$$

wherefore these equations yield

$$\frac{\partial \Delta \eta}{\partial x} = M \frac{d \log \Delta \alpha}{dx} \cdot \Delta c_x,$$

in accordance with the condition (II)¹.

Cornell University. December, 1904.

¹ Richards's conclusions, on p. 307 of his paper: "When the heat capacity of a system does not change during a reaction, and concentration influences are balanced, the free-energy and the total-energy changes of the reaction are equal and unchangeable with the temperature," are consequences of his fundamental assumption,

$$\begin{aligned} \frac{\partial \Delta f}{\partial \theta} &= -M \frac{\partial \Delta e}{\partial \theta} \\ &= -M \cdot \Delta c_x. \end{aligned}$$

For, when $\Delta c_x = 0$, it follows that

$$\frac{\partial \Delta f}{\partial \theta} = \frac{\partial \Delta e}{\partial \theta} = 0,$$

which is the second of the above statements; and, because of

$$\Delta f = \Delta e + \theta \frac{\partial \Delta f}{\partial \theta},$$

it follows that

$$\Delta f = \Delta e,$$

which is the first statement. Both, with the exception of the statement that $\partial \Delta e / \partial \theta = 0$, stand or fall with the fundamental assumption made.