Letters to the Editors

On The Heat of Solution of Oxygen in Uranium Dioxide

The heat and entropy of solution of oxygen in non-stoichiometric uranium dioxide has been calculated from oxygen dissociation pressure curves by Blackburn (1) under the assumption that: (i) the partial molar heat of solution does not depend on the oxygen concentration, and (ii) the entropy of solution is a linear function of the oxygen concentration. The assumption may be easily proved or disproved, on the grounds of the following considerations.

x being the excess oxygen, as defined in the oxidized product formula UO_{2+x}. The above equation, which specifies that proposed by Blackburn,

$$\ln p_{O_2} = a(T) + b(T)x$$

means that in the x versus $1/T$ plot the lines for $\ln p = n$ (or Kn), with n consecutive integers, must be equispaced parallels.

Using the results of Blackburn and those of Aronson and Belle (2), extrapolated by Belle and Lustman (3), the diagram of Fig. 1 has been drawn; the agreement with the forecasts looks at least reasonable. From a least squares fit
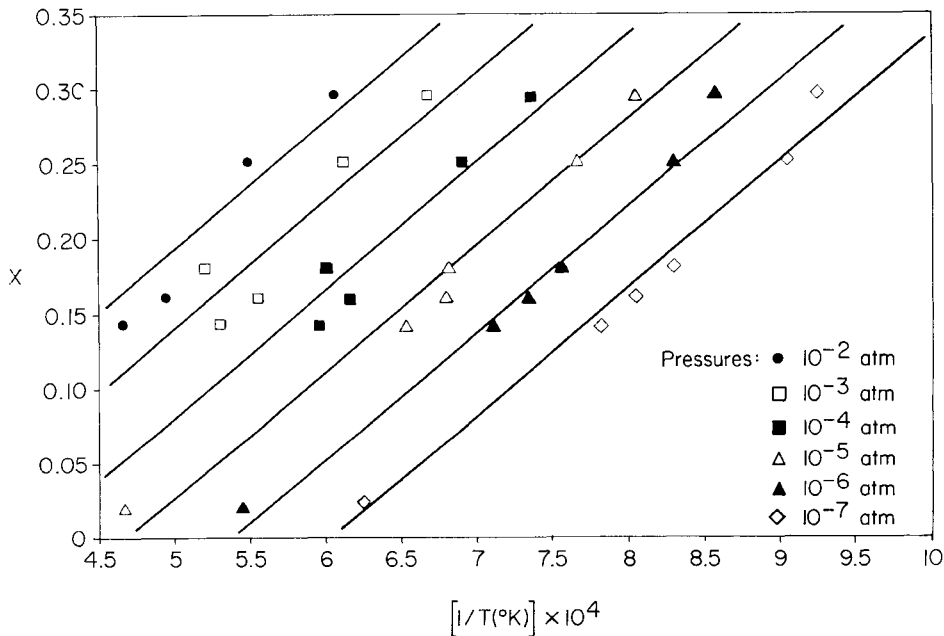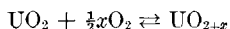

FIG. 1. Oxygen excess vs inverse of temperature at constant pressures

The equilibrium constant for the reaction

$$UO_2 + \tfrac{1}{2}xO_2 \rightleftarrows UO_{2+x}$$

is

$$k_{p(O_2)} = p_{O_2}$$

whence

$$\Delta \bar{F}_{O_2} = -RT \ln p_{O_2}$$

for one mole of O_2. As a consequence, Blackburn's hypothesis may be written

$$\ln p_{O_2} = -\frac{\Delta \bar{F}_{O_2}}{RT} = -\frac{\Delta \bar{H}_{O_2} - T\Delta \bar{S}_{O_2}}{RT} = \frac{A}{T} - B - Cx$$

of the above data, the partial molar heat of solution and entropy change per mole of O_2 are found to be:

$$\Delta \bar{H}_{O_2} = 75{,}150 \text{ cal/mol} \quad \Delta \bar{S}_{O_2} = -3.50 + 182.89x \text{ cal/mol } °K$$

The figure for the partial molar heat of solution is higher than that supplied by Blackburn (58,520 cal/mol), but, singularly enough, in excellent agreement with those given in the more accurate treatments of Aronson and Belle (2) and in the pictures of Miller, Merten, and Porter (4), who consider either the nonstoichiometric material as a solid solution of two oxides of different stoichiometries, or explicitly the changes in the uranium oxidation states, which take place when the oxygen concentration is varied. In fact, they all yield figures between 75,810 and 75,980 cal/mol.

REFERENCES

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3. J. Belle and B. Lustman, WAPD-184 (1957).
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R. L. Colombo

FIAT
Sezione Energia Nucleare
Torino, Italy

On the Derivation of a Variational Principle for Linear Systems

A variational principle due to Roussopoulos (*1*) makes it possible to estimate the weighted average of an arbitrary linear functional of the solution to a given linear operator equation. It can be shown (*2*) that most of the familiar variational principles for linear equations (for example, those used by Marshak, Schwinger, Kourganoff, and Rayleigh) can be derived from Roussopoulos' principle as special cases. However, since it is still necessary to postulate arbitrarily the form of this functional, it is desirable to derive it from simpler or more intuitive considerations. The following is an attempt to do this.

We consider a specified physical system (such as a reactor) whose state is described by a function $\phi(x)$, where x denotes the relevant phase space coordinates of the system (that is, the independent variables such as position, energy, angle, and time). In general, there will be many ways of describing the given system, each with its corresponding state function and associated linear or nonlinear equation which the state function satisfies. While the conventional equations describing neutron diffusion are linear, it is possible to choose a nonlinear description, as in the invariant embedding method of Bellman. On the other hand, a problem such as the propagation of a one-dimensional shock wave in compressible gas dynamics, which seems inherently nonlinear, can be linearized by interchanging the independent and dependent variables as first shown by Riemann. In both cases, the alternative descriptions involve no approximations and are completely equivalent to the original ones; they are, however, more convenient for some purposes.

We shall take the standpoint that our objective in choosing an appropriate description of the system is not primarily to calculate the particular state function ϕ in all its detail; we are interested, instead, in determining a single numerical quantity depending on the state (for example, the absorption rate in a particular region of a reactor, or the multiplication constant). We shall denote this quantity by $F[\phi]$ to indicate that it is a functional of the state description; that is, it depends on the state throughout the system phase space. As yet we have specified neither the state description nor the dependence on the state of the quantity we want to calculate. Regardless of the form of this dependence, however, the quantity can be expanded in a functional power series (*3*)

$$F[\phi] = \sum_{n=0}^{\infty} \frac{1}{n!}$$
$$\cdot \int dx_1 \cdots \int dx_n A_n(x_1 \cdots x_n)\phi(x_1) \cdots \phi(x_n) \tag{1}$$

where the integrations extend over the region in phase space defining the system. The kernels are given by

$$A_n(x_1 \cdots x_n) = \frac{\delta^n F[\phi]}{\delta\phi(x_1) \cdots \delta\phi(x_n)}\bigg|_{\phi=0} \tag{2}$$

and are the nth functional derivatives of F evaluated for $\phi = 0$. (This expansion can be obtained by considering that ϕ is specified at a finite number of points, regarding F as an ordinary function of these variables, expanding it in a Taylor series, and letting the number of points at which ϕ is evaluated become infinite.)

At this point, we shall impose two requirements on this formalism and determine what specializations in the theory they will lead to.

(a) The first requirement is simplicity. We would like to choose a description of the system in such a way that the dependence on the state function, of the number we are primarily interested in, is as simple as possible. To this end, we shall assume that the higher terms in the functional power series are rapidly decreasing and that we can truncate the series after the quadratic term.

(b) The second requirement is insensitivity. That is, we would like the value of F to depend only weakly on its argument so that it will be insensitive to errors made in an approximate calculation of the state function. More formally, we shall require that if a small error $\delta\phi$ is made in the state, the corresponding error δF will vanish to first order.

To determine the consequences of these two requirements, we have to calculate the variation in F from Eq. (1) and set it equal to zero. The result is

$$\delta F = \int dx\, \delta\phi(x)\left[A_1(x) + \int dx' A_2(x, x')\phi(x') \right] = 0. \tag{3}$$

Now since this holds for arbitrary variations of ϕ (provided they are sufficiently small), it follows that ϕ must satisfy the following equation:

$$A_1(x) + \int dx' A_2(x, x')\phi(x') = 0 \tag{4}$$

which is of the form of a general linear inhomogeneous integral equation, with a kernel which is symmetric (since the functional derivatives are symmetric in their arguments) but which is otherwise arbitrary. Suppose now that we use Eq. (4) to simplify the calculation of the functional F by substituting it into the right side of Eq. (1) (the sum now goes only from zero to two). The result is

$$F[\phi] = A_0 + \frac{1}{2}\int dx A_1(x)\phi(x), \tag{5}$$

where ϕ is now the particular function which satisfies Eq. (4).

We thus have the following result: Imposing the requirements of simplicity and insensitivity implies that the theory which has been used to describe the system is equiva-