DE BROGLIE'S CYCLICAL ACTION INTEGRAL

AND

THE THERMODYNAMIC AVAILABILITY FUNCTION

par Joseph F. Mucci *
Theoretical Chemistry Department
Oxford University
Oxford, England

(manuscrit reçu le ler Novembre 1977)

Abstract: Mathematical expressions involving de Broglie's cyclical action integral, A, from his reinterpretation of wave mechanics and the availability function, Λ , are developed. These relationships indicate possible pathways to a deeper insight into the significance of Λ .

Résumé: On propose des expressions mathématiques réunissant l'intégrale d'action cyclique A de de Broglie, appartenant à sa réinterprétation de la mécanique ondulatoire, et la fonction énergie utilisable A. Ces relations indiquent un chemin possible vers une compréhension plus profonde du sens de A.

Ton leave from Department of Chemistry, Vassar College, Poughkeepsie, New York 12601, U.S.A. The author would like to acknowledge the kindness and encouragement of the late Professor C.A. Coulson, F.R.S. in the early stages of this study. In a previous publication (1) we demonstrated the similarity in mathematical form of the entropy, S; the cyclical action integral, A, from de Broglie's reinterpretation of wave mechanics (2) and the average information gained per trial, $\overline{1}$, from information theory (3). We recall the mathematical expressions (1) for these functions:

$$S = -k \sum_{i} p_{i} l_{n} p_{i}$$
 (1)

and

$$\overline{I} = -c \sum_{j} p_{j} \ln p_{j}$$
(3)

where k, h, and c are the Boltzmann, Planck, and a positive constant respectively; p_i is the probability that the system is in state i; and p_j are the assigned probabilities for the possible events as considered in information theory $\binom{1}{3}$.

In this paper we demonstrate the relationship of expressions (1), (2) and (3) to the thermodynamic availability function, Λ , and discuss the significance of these relationships.

One of our goals has been to use the similarity in mathematical form of equations (1), (2) and (3) to find possible routes to a further interpretation of de Broglie's cyclical action integral, A, and the nature of his "hidden thermostat" as part of his reinterpretation of wave mechanics. At this time, we carry the general consideration further by utilizing the availability function, Λ , from thermodynamics and demonstrate its connection to S and in turn to A and $\overline{\mathbf{1}}$. This demonstrated relationship of A to Λ can possibly be utilized to give an additional practical thermodynamic base to the reinterpretation of wave mechanics as developed by de Broglie. Let us proceed with the essential particulars of this study.

We recall a simple but important relationship between the probabilities used in statistical thermodynamics and the avai-

labilities used in classical thermodynamics such that

$$P_{i} = e^{-\beta \Lambda} i \tag{4}$$

where p_i is the probability that a member of a grand canonical ensemble is in state i; $\beta=1/kT$ and Λ_i is the availability corresponding to state i. In addition, the availability has been defined by Keenan (4)(5) as

$$\Lambda_1 = (E_1 + P_0 V_1 - T_0 S_1) - (E_0 + P_0 V_0 - T_0 S_0)$$
 (5)

where Λ_1 , the availability, is the maximum useful work in going from state 1 characterized by P_1 , V_1 , T_1 and E_1 etc. to its environmental state characterized by T_0 , P_0 etc. It is also sometimes helpful to use different forms (4)(5) of equation (5) by substituting other equivalent thermodynamic functions that are appropriate to the system under investigation.

Equation (4) is applicable to any type of ensemble and we can write

$$\Lambda_{i} = -\frac{1}{\beta} \ln p_{i} \tag{6}$$

Using equations (1) and (6) we can write that

$$\frac{s}{k} \circ \beta \sum_{i} p_{i} \Lambda_{i} \tag{7}$$

and likewise using equation (2) we obtain

$$\frac{A}{h} \sim \beta \sum_{i} P_{i} \Lambda_{i}$$
 (8)

Since Jaynes $^{(6)}$ has considered the connection between S and \overline{I} we can apparently write using equations (1), (2), (3), (7) and (8)

$$\frac{S}{k} \sim \frac{A}{h} \sim \frac{\overline{I}}{c} \sim \beta \sum_{i} p_{i} \Lambda_{i}$$
 (9)

Equation (8) therefore gives us a relationship between A and Λ . This can be especially useful because expressions for probabilities and availabilities for several types of ensembles

are well known (7)(8)(9)(10) and can therefore be tabulated. Hence since values of Λ can be readily obtained we have a practical way of calculating trends in the values of Λ appropriate to given states as applied to the corresponding Λ . In addition, these results can also be analyzed as applied to S and T through equations (7) and/or (9).

We are at the present time investigating and utilizing the practical aspects of all these expressions. Needless to say this undertaking requires consideration of several different aspects of the problem as well as performing a number of calculations. At any rate, the significance of this present paper was to point out the route which lead particularly to equation (8) and its implication in this whole field of investigation. We are encouraged by our preliminary studies incorporating these expressions.

REFERENCES

- (1) Mucci, Joseph F., Foundations of Physics, 4, 91 (1974).
- (2) de Broglie, L., Foundations of Physics, 1, 5 (1970).
- (3) Shannon, E.C. and W. Weaver, "The Mathematical Theory of Communication", University of Illinois Press, Urbana, 1949.
- (4) Keenan, J.H., British J. Appl. Phys., 2, 183 (1951).
- (5) Keenan, J.H., "Thermodynamics", M.I.T. Press, Cambridge Mass., 1970.
- (6) Jaynes, E.T., Phys. Rev. 106, 620 (1957).
- (7) McQuarrie, D.A., "Statistical Mechanics", Harper and Row, N.Y., 1976.
- (8) Hatsopoulos, G.N. and J.H. Keenan, "Principles of General Thermodynamics", John Wiley and Sons, Inc., New York, 1965.
- (9) Burnstead, H.A. and R.G. Van Name, (eds.), "The Collected Works of J. Willard Gibbs", Yale Univ. Press New Haven, Conn. 1948.
- (10) Van Wylen, G.L. and R.L. Sonntag "Fundamentals of Classical Thermodynamics" 2nd Ed., John Wiley, N.Y. 1976.