

## The Electron Affinity of Amide Radical and the Chemical Stability of Metal Ammonia Solutions

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## Letters to the Editor

**T**HIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.

### New Units for the Measurement of Radioactivity

E. U. CONDON AND L. F. CURTISS  
National Bureau of Standards, U. S. Department of Commerce,  
Washington, D. C.  
May 20, 1946

**I**T has become the custom to express the strength of radioactive sources in terms of curies. This is an erroneous use of this unit since by original definition the curie is that "amount of radon in equilibrium with one gram of radium"<sup>1</sup> as defined by the Radiology Congress in Brussels in 1910. Therefore, the curie can be used only to represent a rate of disintegration in the radium family. It then represents the disintegration rate of radium or its products in equilibrium. Such a use has been indorsed by the International Radium Commission.

The quantity to be specified in designating the strength of radioactive sources in general is the disintegration rate, determined by the decay constant and the number of atoms of the radioactive isotope in the source. This is simply a number, and therefore to establish a suitable unit the only requirement is to select a convenient number of disintegrations per second and give it a name. In selecting this number, consideration should be given to insure that it can be readily expressed in sub-multiples and multiples by the usual prefixes, kilo, milli, micro, etc. A number which fits this requirement is  $10^6$ . Since the curie was named in honor of M. and Mme. Curie, the co-discoverers of radium, it is natural to select the name "rutherford" for the new unit. The appropriate abbreviation is "rd," which conflicts with the abbreviation of no other well accepted physical unit. The micro-rutherford would become one disintegration per second, a convenient number to remember. Furthermore, the rutherford itself is a small unit of the order of magnitude of many sources used in laboratory measurements. It is sufficiently different in size from the curie that no confusion can arise with the curie in connection with measurements of activities in the radium family. Large sources would require the use of positive powers of ten, which would be preferable to the use of a large unit requiring negative powers of ten.

It should be pointed out that the continued use of the curie for all radio-isotopes not only requires a redefinition of the curie, but in addition the value of the curie is un-

certain to at least 4 percent and values are in current use well outside this limit. The rutherford provides a definite unit. In addition to eliminating the undesirable use of the curie, the proposed unit also eliminates the basic necessity for measuring radio-isotopes in terms of a standard. Any measuring device which will determine the total number of disintegrations per second will provide directly the strength of the source in rutherfords. A counting arrangement for which the solid angle factor is known is an example. Radioactive standards may be used to determine this factor for a given geometrical arrangement, but other methods are also available.

In the measurement of sources of gamma rays, the roentgen has gained increasing use, largely because this unit is independent of the quality (electron volts) of the gamma radiation. There is need for a unit in which the intensity of gamma-ray sources can be expressed to eliminate the use of the curie for this purpose. An obvious unit derived from the definition of the roentgen is a roentgen-per-hour at one meter. The roentgen-per-hour at one meter can be abbreviated r.h.m., which again is not readily confused with any other common abbreviation. It has been suggested that this abbreviation can be pronounced "rum." It should be noted that a gamma-ray source equal to one r.h.m. will have a gamma-ray strength 1.18 times that of 1 curie of radium. Therefore, the roentgen-per-hour at one meter has the same order of magnitude as the curie in the measurement of gamma-ray sources.

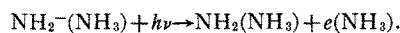
The National Bureau of Standards, at the suggestion of the Committee on Radioactivity of the National Research Council, recommends the general use of these units.

<sup>1</sup> E. Rutherford, "Radioactive Substances and Their Radioactivity" (1913), p. 479. "The Radioactive Constants as of 1930," International Radium-Standards Commission Report, Rev. Mod. Phys. 3, 427 (1931).

### The Electron Affinity of Amide Radical and the Chemical Stability of Metal-Ammonia Solutions

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Department of Chemistry, Stanford University, California  
May 13, 1946

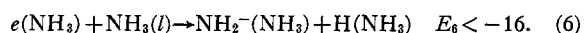
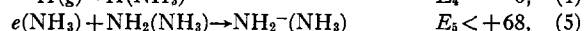
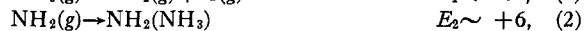
**N**EW experimental studies have been carried out, dealing with concentration and temperature dependence of electrical conductivity and of the near ultra-violet absorption spectrum of liquid ammonia solutions of sodium and potassium amides. These substantiate older observations<sup>1</sup> that the amides behave as weak electrolytes, and indicate that the dissociation constants increase with rising temperature. They also show that the constituent responsible for the yellow color of such solutions is the amide ion,  $\text{NH}_2^-$ . Of particular importance is the observation that light absorption by the amide ion results in a striking photo-conductivity. This fact supports the interpretation of the observed continuous absorption spectrum as an *electron affinity spectrum*,<sup>2</sup> corresponding to the physical process



No over-all photochemical reaction is observed, suggesting

that recapture of conduction electrons by the free amide radicals must be rapid.

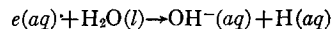
The long wave-length threshold of the amide ion light absorption is at about 4200Å, corresponding to an energy of some 68 kilocalories per mole. This value would appear to represent a *numerical upper limit* for the energy change associated with the above dissociation process. Some related considerations employing Hess' law are of paramount importance in understanding the remarkable chemical stability of metal-ammonia solutions. In the following equations, the inequality signs refer to *algebraic* values of the corresponding reaction energies, given in kilocalories per mole:



Reaction (6), being endothermic by at least 16 kilocalories, must have an activation energy at least as great as this value. Since the dissociation energy of the "first" N-H bond in  $\text{NH}_3$  is without doubt greater numerically than the average value<sup>3</sup> used for reaction (1), a more probable estimate of the minimum activation energy of (6) would be of the order of 30-40 kilocalories per mole. That such large values actually obtain is indicated by the author's observations that highly purified metal-ammonia solutions preserved in sealed vessels at room temperature require several months for practically complete discharge of the characteristic blue color. The probable role of catalysts is to lower the energy deficit of reaction (6) by adsorption of hydrogen atom. In support of this postulate is the fact that the metals most suitable for hydrogenation catalysts

are also the most effective in promoting amide formation in metal-ammonia solutions.

If the far ultraviolet absorption spectrum of aqueous hydroxyl ion<sup>4</sup> is interpreted as an electron affinity spectrum, entirely analogous considerations indicate the reaction



to be considerably *exothermic* and hence probably associated with a negligible activation energy. This affords a ready explanation of the impossibility of preparing aqueous metal solutions containing "solvated" electrons, and suggests that affinity spectra of aqueous negative ions should not be attended by photo-conductivity.

If the solvation energy of conduction electrons in ammonia is estimated as less than 10 kilocalories,<sup>5</sup> then the numerical upper limit for the sum of the electron affinity of amide radical and the solvation energy of amide ion in ammonia is roughly  $68 + 6 + 10 = 84$  kilocalories. Any reasonable estimate of the amide ion solvation energy results in an extremely small electron affinity for the amide radical—of the order of 20-30 kilocalories. Such a value would fall in logical sequence with the respective figures of 95 and 48 kilocalories for the electron affinities<sup>3</sup> of F and OH. So small a value for the electron affinity of amide radical, as compared with the ionization potentials of alkali metal atoms, would suggest that the binding in the alkali metal amides is predominantly *covalent*. The experimentally observed weak electrolyte behavior in liquid ammonia solution supports this view, as do the relatively high volatility and low melting points of the pure substances.<sup>6</sup>

<sup>1</sup> C. A. Kraus, *The Properties of Electrically Conducting Systems* (Chemical Catalogue Company, 1922).

<sup>2</sup> J. Franck and G. Scheibe, *Zeits. f. physik. Chemie* **A139**, 22 (1928).

<sup>3</sup> O. K. Rice, *Electronic Structure and Chemical Binding* (McGraw-Hill Book Company, Inc., New York, 1940).

<sup>4</sup> H. Ley and B. Arends, *Zeits. f. physik. Chemie* **B6**, 240 (1929).

<sup>5</sup> R. A. Ogg, Jr., *J. Chem. Phys.* **14**, 295 (1946).

<sup>6</sup> F. W. Bergstrom and W. C. Fernelius, *Chem. Rev.* **12**, 43 (1933).