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The Stability of Gaseous Nitryl Chloride

Richard A. Ogg Jr. and M. Kent Wilson

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equations:

$$kT\int_1^n \ln\frac{p_s}{p(\nu)}d\nu=a(\sigma_s-\sigma_{sl}), \tag{1}$$

$$a=\frac{kT\int_1^n \ln(p_s/p(\nu))d\nu}{\sigma_{lv}\cos\theta}, \tag{2}$$

where p_s is the saturation pressure of the liquid, $p(\nu)$ is the vapor pressure at which ν molecules of the vapor are adsorbed by a solid of area a, σ_s, σ_{sl}, and σ_{lv} are respectively the interfacial tensions of the solid-vacuum, solid-liquid, and liquid-vapor interfaces and θ is the contact angle. It is believed the theory is fundamentally unsound and the alleged experimental support non-existent.

Equation (1) was obtained by equating the change of free energy, ΔG, of the adsorbate to the change of the available surface energy of the adsorbent. Since these two effects are entirely different, it is not correct to equate the one to the other to obtain Eq. (1). This can be easily demonstrated when the equations for these energy changes are compared. For a single adsorbate at constant temperature,

$$\Delta G=\int \mu d\nu,$$

where μ is the chemical potential; for the adsorbent,

$$\sum_{\substack{\text{all surface}\\ \text{phases}}}\int a d\sigma=-\int \nu d\mu$$

by the familiar Gibbs' equation. Obviously ΔG cannot be identified with $a(\sigma_s-\sigma_{sl})$ as Mizushima has contended.

The transformation of Eq. (1) into (2) by means of du Pré's equation, $\sigma_{vl}\cos\theta=\sigma_s-\sigma_{sl}$, involves another common misconception. The du Pré equation is strictly an equilibrium relation. If a liquid spontaneously spreads on a solid surface, equilibrium evidently does not exist, and the du Pré equation is no longer valid. In such cases it is not permissible to assume that the contact angle is zero, because spontaneous spreading indicates there is *no* contact angle which is quite different from a zero angle. The system toluene-glass used by Mizushima is precisely such a system to which the du Pré equation cannot be applied, because toluene will spontaneously spread on glass. Even granting that it is permissible to apply the du Pré equation to such systems, Mizushima's fourth equation

$$\sigma_{lv}\cos\theta=46.5\ \text{ergs/cm}^2$$

is still untenable, because $\sigma_{lv}\cos\theta$ can never be greater than the surface tension of toluene, which is 27.9 at 25°C. Mizushima attributed the above relation to Bartell and Merrill[2] without realizing that these authors have never used $\sigma_{lv}\cos\theta$ to evaluate the adhesion tension of systems like toluene-glass.

In the application of adhesion tension ($A\equiv\sigma_s-\sigma_{sl}$) it should be noted that A depends not only on the nature of the liquid and the solid, but also on the structure of the solid surface. For instance, against the same liquid the (111) plane of NaCl would undoubtedly give different adhesion tension value than the (100) plane. Even with amorphous substances such as charcoal different samples will often give different A values against the same liquid.[3] It is, therefore, erroneous to assume that when equal areas of two solids of the same chemical composition are compared, they will invariably show identical energy effects. In order to test his theory, Mizushima compared the ΔG value calculated from the adsorption data of Carver[4] with the adhesion tension value of Bartell and Merrill and obtained excellent agreement. Carver's data, however, were obtained with Pyrex glass while the adhesion tension value cited (46.5 ergs/cm^2) was for fused quartz. There is no reason to expect that two such different solids would show the same surface characteristics. Hence these data are not comparable. It is also to be noted that in the adsorption of vapors by plane surfaces at saturation pressure, the change in surface energy is not $a(\sigma_{sl}-\sigma_s)$ but $a(\sigma_{sl}+\sigma_{lv}-\sigma_s)$, because a liquid surface has been created. This factor has not been considered by the author. Furthermore, it is a well-known fact that cleaning agents often roughen glass surfaces to such an extent that the effective surface area may be many times greater than the macroscopic geometric value.[5] Since Carver has subjected his glass to quite drastic treatment, it is very probable that the true area is much greater than the value given in his paper. Hence, Mizushima's ΔG value (44 ergs/cm^2) may be easily in error by many hundred percent.

From the above discussion the only conclusion which seems justified is that the close agreement of the two energy values obtained by Mizushima only serves to reveal the incorrectness of his theory.

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The Stability of Gaseous Nitryl Chloride

RICHARD A. OGG, JR.* AND M. KENT WILSON
Mallinckrodt Chemical Laboratory, Harvard University,
Cambridge, Massachusetts

May 1, 1950

To date there had been no study of thermodynamic properties of nitryl chloride, $ClNO_2$. However, it appears to be a matter of common belief that nitryl chloride cannot be formed in significant amounts from Cl_2 and N_2O_4, and that it does decompose into these substances.[1] The inferences regarding equilibrium are obvious, and would enable estimation of a rough limit for the standard free energy of formation of $ClNO_2$. In studies aimed at structure analysis we have observed the infra-red absorption spectrum of gaseous $ClNO_2$, prepared both by ozonization[1] of ClNO and by the reaction of chlorosulfonic acid with anhydrous nitric acid.[2] (The latter affords a greatly superior preparative method.) The spectrometer and cells were the same as described previously.[3] In the spectral region between 2 and 16μ there are four strong characteristic bands, at approximately 1700, 1340, 1275, and 795 cm^{-1} respectively. These allow ready detection and quantitative estimation of nitryl chloride in gaseous mixtures.

Immediately after preparation, mixtures of gaseous Cl_2 and N_2O_4 (both at partial pressures of the order of 100 mm Hg) displayed only the bands of N_2O_4 and NO_2. On standing at room temperature there was noted the gradual appearance of the above $ClNO_2$ spectrum accompanied by those characteristic respectively of N_2O_5[3] and ClNO. (The latter has two moderately strong bands at approximately 1790 and 920 cm^{-1}.) Concentrations of the various components became practically constant after some ten hours at room temperature. That these final concentrations correspond closely to chemical equilibrium was shown by variation of the initial concentration of Cl_2 and N_2O_4.

It is apparent that equilibrium in the reaction

$$Cl_2+N_2O_4\rightleftharpoons 2ClNO_2$$

is rather slowly attained, but that it corresponds to a much greater stability of $ClNO_2$ than had previously been supposed. Variation of temperature over a considerable range indicated that the formation of $ClNO_2$ by the above reaction is an *exothermic* process. The reaction

$$N_2O_5+ClNO\rightarrow N_2O_4+ClNO_2$$

had previously been studied, using a different method, by Mr. Ralph Weston at Stanford University (these studies will be reported elsewhere), and found to be extremely rapid. It is apparent that this equilibrium is also established in the present system, with comparable concentrations of ClNO and $ClNO_2$.

It was further found that the spectrum of $ClNO_2$ appeared in mixtures of O_2 and ClNO, the rate increasing rapidly with addition of N_2O_4. The equilibrium

$$2ClNO+O_2\rightleftharpoons 2ClNO_2$$

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may at high N_2O_4 concentrations be established much more rapidly than the first equilibrium discussed above.

Quantitative study of the three new equilibria reported here provides an excellent approach to the thermodynamic properties of $ClNO_2$. For practical reasons the third reaction above is the most suited to accurate measurement, but the studies on all three prove to be self-consistent, employing known thermodynamic properties of the other substances involved. As a result of these studies, a provisional value for the energy of dissociation of $ClNO_2$ into Cl and NO_2 of some 32 kilocalories per mole has been found. This figure raises grave doubts regarding the kinetic studies of Schumacher and Sprenger.[1] These authors reported a quasi-unimolecular decomposition of nitryl chloride, this dissociation being considered the rate determining step. However, their measured activation energy was only some 21 kilocalories per mole. It is apparent that the decomposition is vastly more complex than postulated by these authors, and that their studies have no value in discussing theories of quasi-unimolecular reactions.

* Currently on leave from Stanford University, California.

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[2] German Patent 509,405 to Karl Dachlauer.

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Carrier-Free Radioisotopes from Cyclotron Targets. VIII. Preparation and Isolation of $Cu^{64,67}$ from Zinc*

HERMAN R. HAYMOND, ROY D. MAXWELL,† WARREN M. GARRISON, AND JOSEPH G. HAMILTON
Crocker Laboratory, Radiation Laboratory, and Divisions of Medical Physics, Experimental Medicine, and Radiology, University of California, Berkeley and San Francisco, California

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THE radio-copper was produced by bombardment of zinc with 19-Mev deuterons in the 60-in. cyclotron at Crocker Laboratory. At this energy, the longer-lived radioisotopes[1] of copper, $Cu^{64,67}$, are produced in a thick target by the nuclear reactions, $Zn^{64}(d, 2p)Cu^{64}$, $Zn^{66}(d, \alpha)Cu^{64}$, $Zn^{67}(d, 2p)Cu^{67}$. Radioisotopes of gallium are produced concurrently by the reactions, $Zn(d, xn)Ga$. The carrier-free radio-copper was separated from the target element and from the radioisotopes of gallium by a solvent extraction method based on the selective solubility of copper dithizonate in carbon tetrachloride. This procedure,[2] originally developed for the colorimetric determination of microgram quantities of copper, quantitatively extracted $Cu^{64,67}$ from solutions containing less than approximately 10^{-8} g of copper, the minimum detectable by colorimetry under the experimental conditions used.

A block of spectrographically pure[3,4] zinc was soldered to a water-cooled aluminum target and bombarded for a total of 20 μa-hr. at an average beam intensity of 10 μa. Approximately 1.0 g of the bombarded surface was removed by milling and dissolved in a minimum volume of 12*N* HCl. The solution was diluted to 5.5*N* and the gallium activities were extracted with ether after the addition of 10 mg of $GaCl_3$ carrier. The aqueous phase was evaporated almost to dryness, adjusted to *p*H 1.0–1.2 with NaOH to a volume of 50 ml and extracted three times with equal volumes of CCl_4 containing 0.001 percent dithizone. Under these conditions, the carrier-free $Cu^{64,67}$ was quantitatively separated from the target element and from traces of gallium which may not have been completely removed in the previous extraction. The CCl_4 phases were combined, washed twice with 0.1*N* HCl and evaporated to dryness in a porcelain dish. To remove excess dithizone and to destroy the copper dithizone complex, the dish was heated at 500°C for ½ hr. The carrier-free $Cu^{64,67}$ was dissolved in an amount of 0.1*N* HCl which on neutralization gave an isotonic saline solution of the desired volume for subsequent biological investigation.

The radio-copper was identified by half-life determination, absorption measurement, and by chemical separation with carriers. The decay curve was followed for 500 hr. and showed the 12.8-hr. period[5] of Cu^{64} and a longer-lived activity which after 100 hr. leveled off into a 72-hr. period. This activity, presumably Cu^{67},[6] was followed for four half-lives and accounted for approximately 3.0 percent of the total beta-activity corrected to the time of bombardment. Absorption measurements 10 hr. after bombardment showed the 0.6-Mev beta-particle and 1.2-Mev gamma-ray reported[5,7] for Cu^{64}. A tracer amount of activity added to a 1*N* HCl solution of Ni, Cu, and Ga in carrier amounts was quantitatively recovered in the CuS fraction following precipitation with H_2S.

We wish to thank Mr. T. Putnam, Mr. B. Rossi, and the 60-in. cyclotron crew at Crocker Laboratory for bombardments and Professor G. T. Seaborg for helpful suggestions.

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† Lieutenant Colonel, U. S. Army, now stationed at Walter Reed Hospital, Washington, D. C.

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[2] E. B. Sandell, *Colorimetric Determination of Traces of Metals* (Interscience Publishers, Inc., New York, 1944).

[3] The zinc was obtained from Johnson Mathey and Company. Copper was not detected by spectrographic analysis.

[4] The reagents and solutions used in the isolation of Cu^{64} were tested for copper impurity using the method described in reference 2. The water was triple-distilled from glass.

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Errata: The Statistical Mechanical Theory of Transport Processes. III. The Coefficients of Shear and Bulk Viscosity of Liquids

[J. Chem. Phys. **17**, 988 (1949)]

JOHN G. KIRKWOOD, FRANK P. BUFF, AND MELVIN S. GREEN
The Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena 4, California

EQUATION (6) should read

$$\left[\frac{\langle\mathbf{PP}\rangle_{\mathrm{Av}}}{m}-m\mathbf{uu}\right]\rho^{(1)}=\rho^{(1)}kT\mathbf{1}-\frac{\rho^{(1)}kT}{\zeta}\left[\dot{\boldsymbol{\varepsilon}}-\mathbf{1}\frac{\nabla\cdot\mathbf{u}}{3}\right],$$

where $\mathbf{1}$ is the unit tensor. The first term $\rho^{(1)}kT/3\zeta$ in the second of Eqs. (10) defining bulk viscosity should be omitted. Likewise, the first term $NmkT/3v\zeta$ of Eq. (45) should be omitted. In the first line of Eq. (16), $\nabla\mathbf{p}_1$ should be changed to $\nabla\mathbf{R}_1$. In the last line of Eq. (36), $I(z)$ should read $I_\alpha(z)$. In the first line of reference 2, the date should be changed from 1945 to 1943.

The change in Eq. (6) removes kinetic energy transport terms from the bulk viscosity, which in any event, are negligible in liquids, for which the theory is designed. The intermolecular force contribution to bulk viscosity remains unaffected by the change.

The change in Eq. (6) is necessitated by the definition of temperature in the non-equilibrium case

$$\langle\Pi^2\rangle_{\mathrm{Av}}=3mkT$$

and the retention of ${}^{(1)}\mathbf{F}\dagger$, as yet undetermined by our theory, in Eq. (15), which should read

$$\begin{aligned}\langle\mathbf{\Pi\Pi}\rangle_{\mathrm{Av}}-mkT\mathbf{1}=\frac{m}{2\zeta}\Big[&\langle\mathbf{\Pi\Pi}\rangle_{\mathrm{Av}}\cdot\nabla\mathbf{u}+\langle\mathbf{\Pi}\cdot\nabla\mathbf{u}\mathbf{\Pi}\rangle_{\mathrm{Av}}+\mathbf{u}\cdot\nabla\langle\mathbf{\Pi\Pi}\rangle_{\mathrm{Av}}\\&+\frac{\partial\langle\mathbf{\Pi\Pi}\rangle_{\mathrm{Av}}}{\partial t}-\langle{}^{(1)}\mathbf{F}\dagger\mathbf{\Pi}\rangle_{\mathrm{Av}}-\langle\mathbf{\Pi}\,{}^{(1)}\mathbf{F}\dagger\rangle_{\mathrm{Av}}\Big]\end{aligned}$$

$$\rho^{(1)}\langle{}^{(1)}\mathbf{F}\dagger\mathbf{\Pi}\rangle_{\mathrm{Av}}=N\int^{(1)}\mathbf{F}\dagger\mathbf{\Pi}f^{(1)}d\mathbf{p}.$$

By taking the trace of both sides of the corrected form of Eq. (15), we obtain

$$\frac{\partial T}{\partial t}+\mathbf{u}\cdot\nabla T+\frac{2}{3}T\nabla\cdot\mathbf{u}-\frac{2}{3mk}\mathrm{Tr}\langle{}^{(1)}\mathbf{F}\dagger\mathbf{\Pi}\rangle_{\mathrm{Av}}=0$$

and are led to the corrected form of Eq. (6).

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