

shown curves illustrating the selective adsorption of SF_6 from a 50% air and 50% SF_6 mixture. The SF_6 adsorption characteristics of the sieve are found to be independent of the air concentration. The SF_6 commercially available contains impurities of CF_4 , O_2 , N_2 , A and H_2O . With the exception of water, and slight amounts of nitrogen, the other impurities are not adsorbed by the sieve and thus this provides a means for purifying SF_6 . Mild heating removes the SF_6 and not the water. The SF_6 interacts through an induced dipole whereas water adsorbs by dipolar interaction.

THE HEAT OF FORMATION OF CF_2

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Available data for the heat of formation of CF_2 are based on the general analogy of the C-F system with the C-H system² or on rates of reaction of Na with fluorinated methanes,³ and suggest $\Delta H_f^\circ \leq -18$ kcal./mole. No lower limit on the heat has been suggested. Margrave⁴ has concluded recently from a mass spectrometric study of C_2F_4 and the appearance potential of CF_2^+ that $\Delta H_f^\circ \approx -30 \pm 10$ kcal./mole.

Further evidence regarding CF_2 has been deduced by determining the lowest temperature at which CF_2 bands may be detected in absorption in the system CF_4 -graphite.⁵ The first faint, but clearly visible bands (2487 and 2457 Å.) appear at 1830°K. from the reaction $\text{CF}_4(\text{g}) + \text{C}(\text{s}) = 2\text{CF}_2(\text{g})$ with $P_{\text{CF}_4} = 0.18$ atm. From the very diffuse nature of the bands, it is likely that a minimum of 0.0015 mm. of CF_2 at 1800°K. is required for detection, while the maximum amount is probably 0.015 mm. at 1800°K., depending on the transition probability. These pressures, along with the known heat of formation of $\text{CF}_4(\text{g})$,⁶ and other standard thermodynamic functions, lead one to calculate $\Delta H_f^\circ(\text{CF}_2) \leq -30$ kcal./mole at 298°K.

A comparison also can be made with the Si-Cl system for which Schafer and Nickl⁷ have reported the heat of formation of the analogous molecule SiCl_2 as -30 kcal./mole. One can compare the heat of atomization of SiCl_2 (192 kcal./mole) with the heat of atomization of SiCl_4 (365 kcal./mole) and establish the ratio

$$\frac{\Delta H_a(\text{MX}_2)}{\Delta H_a(\text{MX}_4) - \Delta H_a(\text{MX}_2)} = 1.11$$

A similar value for this ratio appears to hold for the Si-F system.⁸ If exactly the same ratio holds

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for the C-F system, $\Delta H_a(\text{CF}_2) = 243$ kcal./mole and $\Delta H_f^\circ(\text{CF}_2) = -36$ kcal./mole.

Thus, it appears that the heat of formation of $\text{CF}_2(\text{g})$ is considerably more negative than previously thought with the correct value in the range -35 ± 10 kcal./mole.

REACTION OF ATOMIC HYDROGEN WITH SOLIDS AT -195° ¹

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This work was started with the idea of synthesizing LiH_3 . The fundamental notion is that negative ions tend to grow in order to give more room for the electronic cloud and consequently one might expect, given proper conditions, that the proton in lithium hydride could incorporate two hydrogen atoms to form the ion H_3^- . The method used was that developed by Klein and Scheer² in which hydrogen atoms react with various substances frozen on a liquid nitrogen-cooled surface. Our results (largely negative) are shown in Table I.

TABLE I
ACTION OF ATOMIC HYDROGEN ON VARIOUS SUBSTANCES
UNDER VARIOUS TEMPERATURES

Substance	Temp., °C.	Results
Li	-195	No reaction
Li	100	Fast reaction
Na, Hg, Cd, Mg		
Zn, Bi, Ge, Ga	-195	No reaction
Ca	-195	Very slow reaction
Ba	-195	H atoms go to H_2 which is absorbed. No further reactions
	100	
Cu	-195	Apparently an unstable hydride first forms and then decomposes as concn. increases
HN_3	-195	Very slow reaction
HN_3	-150	Very slow reaction
COS	-195	Very slow reaction
Acetic anhydride	-195	No reaction
<i>n</i> -Butylamine	-195	No reaction
Isobutylamine	-195	No reaction
Ethyl alcohol	-195	No reaction
Amyl alcohol	-195	No reaction
Acetone	-195	Very slow reaction
<i>n</i> -Propyl alcohol	-195	Very slow reaction
Carbon tetrachloride	-195	Very slow reaction
Isobutyl alcohol	-195	Slow reaction
<i>sec</i> -Butyl alcohol	-195	Slow reaction
<i>t</i> -Butyl alcohol	-195	Slow reaction
<i>n</i> -Butyl alcohol	-195	Slow reaction (faster than the three previous)
Ethyl iodide	-195	Fast reaction

To our very great surprise, ethyl iodide reacts readily with hydrogen atoms at -195° ; the white solid turns orange and gives a positive test for free iodine using starch indicator. We positively

- (1) Presented at the Fifth International Symposium on Free Radicals, Uppsala, Sweden, July, 1961.
- (2) R. Klein and M. D. Scheer, *J. Phys. Chem.*, **62**, 1011 (1958).

identified ethane, both by the mass spectrometer and gas chromatography, in the fraction removed at -80° , which seems to consist only of ethane. In addition a yellow non-volatile solid remained, which we did not identify.

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STUDIES OF THE COPPER(II)-ALANINE AND PHENYLALANINE SYSTEMS IN AQUEOUS SOLUTION. DISSOCIATION AND FORMATION CONSTANTS AS A FUNCTION OF TEMPERATURE¹

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Many formation constant data have been reported for metal ion-amino acid systems at a single temperature.^{3,4} The copper(II)-alanine,³⁻⁵ and the copper (II)-phenylalanine^{3,4,6} systems have been studied and formation constants reported at 25° and various ionic strength values. However, few studies of the temperature dependence of the formation constants of metal ion-amino acid systems, and, it appears, no data for the reaction of Cu^{++} with alanine or phenylalanine at temperatures other than 25° have been reported.

pK_D values are known at various ionic strengths for the stepwise dissociation of protons from protonated alanine at 0° ,⁷ 20° ,⁷ and 1.0, 12.5, 25, 37.5 and 50° ,⁸ and from protonated phenylalanine at 20° ³ and 25° .⁹⁻¹² ΔH° values at 25° for the stepwise proton dissociation from protonated alanine have been determined by a calorimetric method¹³ and from the temperature dependence of the equilibrium constants.^{7,8}

This paper presents equilibrium constants calculated to infinite dilution for the stepwise reaction of copper(II) ion with alanate and phenylalanate ions, and for the stepwise dissociation of protons from protonated alanine and phenylalanine at 0, 10, 20, 30 and 40° . From the temperature

dependence of these constants, ΔH° values for the reactions are calculated. ΔS° values are calculated from ΔH° and ΔF° values.

Experimental

Procedure.—The pH titrations were made in solutions of low ionic strength in a manner similar to that described previously for the Cu^{++} -acetylacetone system.¹⁴ Titrations were performed with a Beckman Model GS pH meter employing glass and saturated calomel electrodes.

Reagents.—A stock copper(II) perchlorate solution was prepared by dissolving C.P. CuO wire in a concd. HClO_4 - HNO_3 mixture, precipitating $\text{Cu}(\text{OH})_2$ with NaOH solution, washing with water, and dissolving in HClO_4 of known concentration. The solution was standardized with respect to Cu^{++} by conventional analytical procedures. Stock ligand solutions were prepared by dissolving weighed quantities of C.P. alanine and phenylalanine in water.

Buffers.—Bates¹⁵ has summarized and discussed the work of the National Bureau of Standards in determining pH values of standard reference solutions for use in pH titrations. Buffer solutions used in the present study were prepared by dissolving the C.P. salts, potassium hydrogen phthalate (pH 4)¹⁶ and a KH_2PO_4 - Na_2HPO_4 mixture (pH 7),¹⁷ in the required amounts of water and standardizing by conventional means to give solutions equivalent to those whose pH values have been determined from e.m.f. measurements by the National Bureau of Standards.

Calculations.—Molarity quotients for ligand-proton dissociation were determined by pH titration of two portions of each ligand solution with HClO_4 and NaOH , respectively. Molarity quotients for the stepwise reaction of each ligand with Cu^{++} were determined from \bar{n} and free ligand concentration by the method of Block and McIntyre.¹⁸ Thermodynamic equilibrium constants were calculated from the molarity quotients using a modified form of the Debye-Hückel equation.¹⁹ The calculations were made with an IBM 650 computer.

Results

Thermodynamic pK_{Dn} values for proton dissociation from the ligands and $\log K_n$ values for stepwise complex formation of each ligand anion, L^- , with Cu^{++} are given in Table I, together with ΔH°_n and ΔS°_n values calculated from the equilibrium constants. Comparison data from the literature are provided where these were determined under experimental conditions of temperature and ionic strength similar to those used here.

Plots of $1/T$ vs. pK_{D2} and $\log K_n$ are linear; however, the corresponding plot of $1/T$ vs. pK_{D1} in the case of each ligand shows curvature. The causes of this curvature which is observed in many carboxylic and related acids have been discussed by Gurney.²⁰

Discussion

$\log K_1$ is greater for the $\text{Cu}(\text{II})$ -alanine than for the $\text{Cu}(\text{II})$ -phenylalanine system, whereas the values of $\log K_2$ are close together and slightly greater for the copper(II)-phenylalanine. The first formation constant for the $\text{Cu}(\text{II})$ -alanine system might be expected to be greater than that for the phenylalanine system due to the greater basicity of the alanate ion (Table I); however, the relative

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(2) (a) To whom inquiries concerning this article should be sent; (b) taken in part from the M.S. Thesis of Jay W. Wrathall.

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