tion of Sn–H bonds. The reaction products were apparently mixtures, containing no detectable amount of triphenylstannane.

Acknowledgment.—The author is grateful to Dr. Eugene G. Rochow for helpful discussions and advice, and to the National Science Foundation for financial support.

MALLINCKRODT CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.

COMMUNICATIONS TO THE EDITOR

THE SYNTHESIS OF AN ARGINYL PEPTIDE

Sir:

The synthesis of peptides containing arginine has presented unusual difficulties, and only a few dipeptides have been reported. No peptide in which the carboxyl group of arginine is linked to another amino acid has been synthesized.[1] It has now been found that the pyrophosphite method[2] can be used for this purpose.

Carbobenzoxy-L-arginine hydrobromide[3] (0.010 mole) and methyl L-leucinate (0.010 mole) were added to 7 cc. of diethyl phosphite, then tetraethyl pyrophosphite (0.020 mole) was added. After 30 minutes heating on a steam-bath, methyl carbobenzoxy-L-arginyl-L-leucinate hydrobromide hydrate was precipitated as a gum by 100 cc. of anhydrous ether. This was crystallized by dissolving in 5 cc. of methanol, bubbling in hydrogen bromide a moment, then adding 40 cc. of anhydrous ether; yield 3.06 g. (57%). A further 0.47 g. was obtained from the original filtrate on dilution with ether, giving 3.53 g. in all (66%). Solution in 10 cc. of methanol and dilution with 40 cc. of water yielded 2.79 g. (52%), m.p. 90–92°,[4] $[\alpha]^{23}_{\mathrm{D}}$ $-20.3°$ (c 2, methanol).

Anal. Calcd. for $C_{21}H_{36}N_5O_6Br$: C, 47.2; H, 6.79; N, 13.1; Br, 15.0. Found: C, 47.4; H, 6.99; N, 13.3; Br, 15.2.

Carbobenzoxy-L-arginyl-L-leucine was obtained by heating 2.83 g. of the methyl ester hydrobromide hydrate on a steam-bath in 28 cc. of N hydrobromic acid for an hour, making slightly alkaline with ammonium hydroxide and chilling. The crystalline product was recrystallized from 30 cc. of $N/6$ hydrobromic acid by the addition of ammonium hydroxide; yield 1.20 g. (54%), m.p. 223–224° dec., $[\alpha]^{24}_{\mathrm{D}}$ $-26°$ (c 2, 0.4 N HBr). *Anal.* Calcd. for $C_{20}H_{31}N_5O_5$: C, 57.0; H, 7.41; N, 16.6. Found: C, 57.2; H, 7.64; N, 16.6.

L-Arginyl-L-leucine hydrobromide hydrate was obtained by hydrogenation with a palladium catalyst of 1.06 g. of the carbobenzoxy derivative in 40 cc. of water plus 2.5 cc. of 1.04 N HBr. A crystalline product obtained by evaporation of the filtered solution under vacuum was washed out with acetone, then recrystallized by dissolving in 4 cc. of water and slowly adding 40 cc. of acetone; yield 0.78 g. (80%), m.p. 162–163° dec., $[\alpha]^{24}_{\mathrm{D}}$ $+8.6°$ (c 2, water).

Anal. Calcd. for $C_{12}H_{28}N_5O_4Br$: C, 37.3; H, 7.3; N, 18.1; Br, 20.7. Found: C, 37.1; H, 7.2; N, 18.2; Br, 20.7.

Paper chromatography gave an R_f value of 0.58 in a butanol–water–acetic acid (5:4:1) system, and showed the presence of arginine and leucine in an acid hydrolysate.

CHEMOTHERAPY DIVISION
STAMFORD RESEARCH LABORATORIES
AMERICAN CYANAMID COMPANY GEORGE W. ANDERSON
STAMFORD, CONNECTICUT

RECEIVED SEPTEMBER 2, 1953

---

[1] J. S. Fruton, "Advances in Protein Chemistry," Vol. V, Academic Press, Inc., New York, N. Y., 1949, p. 64.

[2] G. W. Anderson, J. Blodinger and A. D. Welcher, THIS JOURNAL, **74**, 5309 (1952).

[3] Prepared by R. Janice Joyce, of these laboratories; m.p. 177–179.5°, $[\alpha]^{24}_{\mathrm{D}}$ $-6.9°$ (c 2, water); calcd. for $C_{14}H_{21}N_4O_4Br$: 20.8% Br. Found: 20.6% Br.

[4] Melting points were taken on a calibrated Fisher–Johns block.

TWO DIMENSIONAL PHASE TRANSITION OF ETHANE ON SODIUM CHLORIDE

Sir:

The chief evidence for first-order phase transitions of films adsorbed on solid surfaces has been the adsorption isotherms measured by Jura, *et al.*, for n-heptane on graphite,[1] ferric oxide[2] and reduced silver powder.[3] Adsorption isotherms for n-heptane on the same solids (but not the same samples) have subsequently been repeated by Smith[4] and by Young, Beebe and Bienes,[5] who report that their work provides no evidence of first-order phase transitions in those systems. Their papers support the trend to interpret all experimentally observed discontinuities in adsorption isotherms as caused by slow rates or diffusion inside the sample or errors in the apparatus.

The chief remaining evidence for a first-order phase transition of an adsorbed film on a solid surface now devolves on the adsorption isotherms of ethane on sodium chloride and on potassium chloride crystals at 90°K., reported by Ross and Boyd,[6] and since verified in this laboratory on a different sample of sodium chloride at 90°K. by Mr. W.

---

[1] G. Jura, W. D. Harkins and E. H. Loeser, *J. Chem. Phys.*, **14**, 344 (1946).

[2] G. Jura, E. H. Loeser, P. R. Basford and W. D. Harkins, *ibid.*, **14**, 117 (1946).

[3] Jura, *et al.*, *ibid.*, **13**, 535 (1945).

[4] R. N. Smith, THIS JOURNAL, **74**, 3477 (1952).

[5] D. M. Young, R. A. Beebe and H. Bienes, *Trans. Faraday Soc.*, **49**, 1086 (1953).

[6] S. Ross and G. E. Boyd, "New Observations on Two-Dimensional Condensation Phenomena," MDDC Report 864, 1947.

Winkler. In spite of the success of certain conclusions drawn by Ross,[7] based on the hypothesis that the observed discontinuity is due to a first-order transition, the evidence lacked the important further authority that could be provided by results at different temperatures. This communication reports the adsorption isotherms of ethane on sodium chloride crystals at 136.0, 131.3 and 122.9° K. These isotherms confirm the existence of a discontinuity and strongly support its interpretation as a first-order phase transition. Figure 1 shows the three isotherms. The isotherm at 122.9°K., with its marked vertical discontinuity, is still below the "two-dimensional critical temperature." The isotherm at 131.3°K. has a much shorter discontinuity that indicates its proximity to the critical temperature. The isotherm at 136.0° K. has no instantaneous vertical slope,[8] and is above the critical temperature. These three isotherms therefore show critical temperature phenomena in the behavior of the adsorbed film of ethane on sodium chloride.

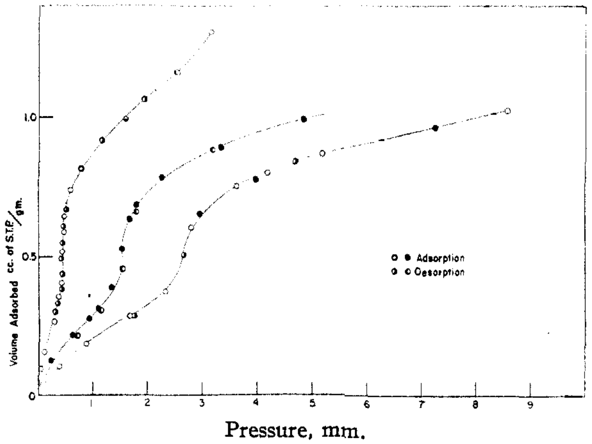

Fig. 1.—Adsorption and desorption of ethane on cube crystals of sodium chloride, at 122.9, 131.3 and 136.0°K.

The two-dimensional critical temperature of ethane on sodium chloride is less than half of the normal three-dimensional critical temperature. This type of behavior has been described by de Boer,[9] as to be expected from the introduction of an induced dipole moment on the ethane molecule from the ionic surface. To cause such a lowering of the two-dimensional critical temperature, the dipoles must be oriented parallel to each other. A diagram illustrating the arrangement of the condensed phase of ethane on a sodium chloride substrate was published by Ross[7] in 1948, and embodies an implicit prophecy of this requirement. Each molecule of ethane is depicted on the crystal lattice in an identical position with respect to the surrounding positive and negative ions. The induced dipoles would therefore necessarily be parallel to one another.

Experimental.—The sodium chloride sample was prepared by the method of Craig and McIntosh.[10] The temperature control was effected by a cryostat based on a design by J. A. Morrison.[11] The ethane was Matheson Research Grade, further purified by passing through *Ascarite* and concd. H_2SO_4 and then fractionated twice into a storage bulb.

---

[7] S. Ross, This Journal, **70**, 3830 (1948).

[8] J. R. Partington, "Advanced Treatise on Physical Chemistry," Vol. I, Longmans, Green and Co., London, 1949, p. 628.

[9] J. H. de Boer, "The Dynamical Character of Adsorption," Clarendon Press, Oxford, 1953, pp. 168–169.

[10] A. Craig and R. McIntosh, *Can. J. Chem.*, **30**, 448 (1952).

[11] J. A. Morrison, private communication.

Department of Chemistry
Rensselaer Polytechnic Institute
Troy, N. Y.
Hadden Clark
Sidney Ross

Received October 28, 1953

LONG RANGE MIGRATION OF CHEMICAL ACTIVITY IN THE SOLID STATE

Sir:

In a study of the chemical effects of the irradiation *in vacuo* of solid polyethylene in the heavy water pile of the Argonne National Laboratory, it has been found that the concentration of vinylidene groups, of which the total unsaturation of the unirradiated polyethylene is constituted—one vinylidene group per molecule—decreases linearly with time of irradiation while simultaneously the concentration of *trans*-vinylene groups increases. These results as estimated from infrared absorption studies are shown in Fig. 1.

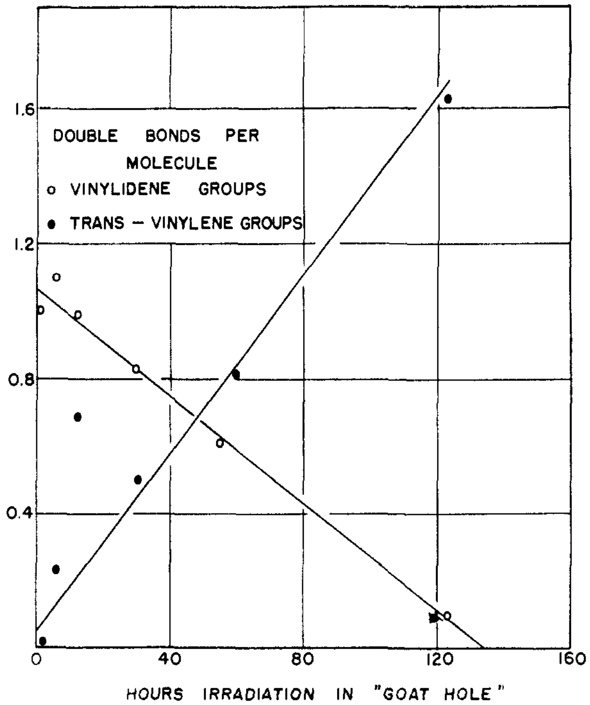

Fig. 1.

As there exists in this type of polyethylene only one vinylidene group per 2300 carbon atoms, the statistical probability of the vinylidene group being affected by the incident radiation is only two in 2300; yet the results indicate that one vinylidene group is eliminated for every 3.6 molecules of hydrogen evolved. To explain this interesting fact the hypothesis of the long range migration of chemically active centers in the polyethylene is postulated.

These chemically active centers may be either hydrogen atoms which must be produced in large