TABLE V.—FIXATION OF PHOSPHORIC ACID, AMMONIA AND POTASH.

Depth of soils.	Phosphoric acid retained. Per cent.	Ammonia retained. Per cent.	Potash retained. Per cent.
6	99.43	99.84	98.55
4	....	98.13	94.18
3	91.25	....	....
2	....	86.12	82.03
1	53.35	50.21	69.19

These results have a great practical bearing on plantation work in these islands. Many of the plantations depend upon irrigation entirely, and a great deal of the water, as I have shown in an article in the August number of the *Hawaiian Planter's Monthly* on "The Water-Holding Power, and the Irrigation of Hawaiian Soils," passes directly and immediately through the soils. In other cases, as in the Hilo district, the soils are subjected to very heavy rains. Were the soluble fertilizer ingredients not fixed at once the loss would be very great; but the experiments show that even under heavy washings they are fixed very rapidly. But the solubility of these substances in water after the first irrigation, though slight, emphasizes the importance of keeping the irrigation well under control. The nitrogen of sulphate of ammonia is gradually changed to nitrate, and most of that which the plant has not assimilated is washed away by the first irrigation or heavy rainfall. The phosphoric acid is more firmly bound, and the loss of this substance is very slight. Under the conditions of the tests, 19 per cent. of the potash applied as sulphate was washed below 6 inches by eight irrigations.

We thus see that heavy and repeated irrigations wash out the available ammonia and potash; and this will partially account for the fact that very often the effects of a fertilizer, especially of a nitrogenous fertilizer, are not lasting.

HONOLULU, H. I.

A PROBABLE CAUSE OF THE DIFFERENT COLORS OF IODINE SOLUTIONS.

BY ARTHUR LACHMAN.

Received September 30, 1902.

IT is a well-known fact that solutions of free iodine have different colors, depending in some way upon the nature of the solvent.

Gautier and Charpy,[1] who investigated this problem about twelve years ago, distinguished four sets of colors, of the following types:

(1) Violet, *e. g.*, chloroform; (2) red, *e. g.*, ethylene bromide; (3) red-brown, *e. g.*, toluene; (4) brown, *e. g.*, alcohol.

A large number of solvents were thus classified, but the authors confessed themselves unable to find any relations between the chemical function of the solvent and the color. The following year, Rigollot[2] determined the absorbing power of different iodine solutions for definite light-waves; but his results led to no explanation. A few years later, an elaborate study of the problem was undertaken by Krüss and Thiele[3] They ascertained the molecular weight of iodine in various solvents, and found that practically in all cases, where moderately dilute solutions were taken, the iodine molecule consists of 2 atoms. Variations from this value were irregular, both for brown and for violet solutions. Concentrated solutions usually gave high molecular weights, indicating association, but no change of color accompanied this association.

In spite of these results, Krüss and Thiele attempt to explain the different colors by an assumption of different molecular weights: violet solutions containing I_2, brown solutions $(I_2)_n$, n being greater than 1. These complicated molecules, however, are supposed to give a normal molecular weight by all osmotic methods. This explanation is equivalent to saying that in brown solutions the molecular weight of iodine is much greater than in violet, but that none of our present methods are able to demonstrate the increase; and it involves a conception of the molecular theory whose utility yet remains to be shown. The change from brown into violet is ascribed to dissociation; if the above theory is correct, solvents with brown color should have less dissociating power than those with violet. But this is contradicted by well-established facts; alcohol has much greater dissociating power than chloroform or benzene.

Notwithstanding the negative results of Gautier and Charpy, and of Krüss and Thiele, a simple causal connection seems to exist between the chemical behavior of the solvent and the color

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[1] *Compt. Rend.*, **110**, 189; **111**, 645 (1890).

[2] *Ibid.*, **112**, 38 (1891).

[3] *Ztschr. anorg. Chem.*, **7**, 25 (1894).

of iodine solutions. This relationship was not apparent to the above investigators *because in critical cases they observed wrong colors,* owing to impurities in the solvents. From the table given below, it will be seen that iodine solutions, when made with pure solvents have but two colors—violet and brown—with but one exception, which will be discussed below.

COLOR OF IODINE IN VARIOUS SOLUTIONS.

A. Violet Solutions.

- Hydrocarbons :
  - Hexane
  - Benzene (thiophene free)
  - Toluene[1]
  - *o*-Xylene[2]
  - *m*-Xylene
  - *p*-Xylene
- Halogen compounds :
  - Chloroform
  - Ethylene chloride[3]
  - Ethylidine chloride
  - Tetrachlorethylene[4]
  - Carbon tetrachloride
  - Isobutyl chloride[5]
  - Amyl chloride
  - Chlorbenzene
  - Benzalchloride
  - Benzotrichloride
  - Bromoform
  - Ethylene bromide[5,6]
  - Trimethylene bromide
  - Amyl bromide[5]
  - Brombenzene
- Nitro compounds :
  - Nitroethane
  - Nitropropane
  - Tetranitromethane
  - Isobutyl nitrate
- Sulphur compound :
  - Carbon bisulphide

B. Brown Solutions.

- Iodides :
  - Ethyl iodide
  - Amyl iodide
  - Cetyl iodide
  - Phenyl iodide
  - Potassium iodide } In water
  - Hydrogen iodide } solutions

Oxygen compounds.

- Alcohols :
  - Methyl alcohol
  - Ethyl alcohol
  - *n*-Butyl alcohol
  - Dimethylethyl carbinol
  - Heptyl alcohol
- Ethers :
  - Ethyl ether
  - Dimethyl acetal
  - Anisol
  - Phenetol
- Ketones :
  - Acetone
  - Methylethyl ketone
  - Diethyl ketone
  - Acetaldoxime
  - Acetophenone
- Acids and esters :
  - Formic acid
  - Acetic acid
  - Lactic acid
  - Caproic acid
  - Ethyl acetate
  - Amyl acetate
  - Isobutyl isobutyrate
- Sulphur compounds :
  - Amyl mercaptan
  - Thiophene

Nitrogen compounds.

- Nitriles :
  - Acetonitrile
  - Propionitrile
  - Capronitrile
  - Benzonitrile
- Nitrilo-bases :
  - Pyridine
  - Quinoline

[1] Gautier-Charpy, red-brown.

[2] Thiele-Krüss, wine-red (xylenes not separated).

[3] Gautier-Charpy, Krüss-Thiele, red.

[4] Tetra-chlorethylene, C_2Cl_4, is the only substance in the above list which is unsaturated in structure. Its easy formation during chlorination reactions indicates that its unsaturated character is more formal than real, in spite of its double bond.

[5] Ethylene bromide, amyl bromide, and isobutyl chloride required careful purification before giving violet solutions. The impure solvents, which gave red solutions, all decolorized permanganate.

[6] Gautier-Charpy, Krüss-Thiele, red.

From the results tabulated above, all of which have been verified personally, the relationship between color and the constitution of the solvent stands out clearly: *saturated solvents give violet, solvents which have unsaturated character give brown solutions.* In the first, or violet class, we find hydrocarbons, their chlorides and bromides, and carbon bisulphide; and also, strange to say, the *nitro compounds.* All the other oxygen compounds, so far as investigated, give brown solutions. The brown solvents comprise the alcohols, ethers, ketones, acids and esters; nitriles and nitrilo-bases; alkyl and other iodides; and bivalent sulphur compounds.

The iodine molecule, as found in iodine vapor, is violet; we have every reason for assuming that in its violet solutions iodine is in a state of normal physical distribution. On the other hand, certain of the brown solutions are known to contain periodides, usually of the form $(MX).I_2$; among these are potassium iodide, phenyl iodide, and the tertiary bases. Nitriles have long been known for their additive properties in general; and in the case of oxygen compounds, the recent startling results of Baeyer and Villiger[1] have fully demonstrated the hitherto unsuspected additive powers of combined oxygen atoms. It seems quite justifiable to assume in all brown iodine solutions the existence of (probably unstable) addition products whose general composition is

$$\text{Molecule-solvent} + I_2.$$

Such an explanation was indeed offered some years ago by Beckmann,[2] and considered and rejected by Krüss and Thiele. If it is assumed, as it was by Beckmann, that the *whole* of the iodine thus adds to the solvent, the effect upon the *observed* molecular weight would be a marked decrease (as a consideration of Raoult's formula shows), contrary to the measurements of Krüss and Thiele. But there is no need to make this assumption; a very small amount of alcohol suffices to change the color of an iodine-chloroform solution, and 3 per cent. of alcohol give as dark a brown as can be obtained with pure alcohol.

EFFECT OF ABSOLUTE ALCOHOL ON COLOR OF IODINE IN CHLOROFORM.

Alcohol. Per cent.	Color.
3.5	Brown
0.4	Red
0.2	Mixed red and violet
0.1	Violet

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[1] *Ber. d. chem. Ges.*, **34**, 2679 (1901).

[2] *Ztschr. phys. Chem.*, **5**, 76 (1889).

The iodine in brown solutions is therefore probably in a condition of equilibrium between pure solution and the addition product

$$\text{Solvent} + I_2 \rightleftarrows (\text{Solvent} + I_2),$$

very much like many double salts, or like the chlorine ions[1] in green chromium chloride hexahydrate.

The view here presented, that brown solutions contain some addition product, and violet solutions simple iodine molecules, is borne out by an important fact: Brown solutions tend to become violet when heated, and conversely, violet solutions become brown on being cooled sufficiently.[2] As heat produces dissociation, and cold induces association, the facts are in excellent agreement with expectation.

The actual isolation of the addition products of iodine with oxygen compounds will probably be difficult, but an effort in this direction will be made as soon as possible. Schützenberger[3] has described an addition product of bromine and ether, and iodine may behave similarly.

Two points remain for discussion. In the first place, the behavior of the nitro compounds seems to put them apart from other oxygen compounds. The structure of the nitro group is still uncertain, but numerous reactions show that its oxygen atoms are quite active, and possess considerable additive power.[4] Their indifference to iodine will be investigated more closely later on.

The second point is the behavior of ethyl bromide towards iodine. In spite of numerous efforts, I have not been able to prepare this substance in a state sufficiently pure to obtain with it a violet iodine solution; in every case, the solution is dark red. Ethyl bromide is made by two methods; the distillation of ethylsulphuric acid with potassium bromide also forms ether, which cannot be separated by the most careful fractioning; and the action of phosphorus bromide upon alcohol yields ethyl bromide contaminated with phosphorus, which resists hours of boiling with moist sodium amalgam. I am confident, however, that ethyl bromide will prove no exception to the above classification of

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[1] Werner: *Ber. d. chem. Ges.*, **34**, 1579 (1901).

[2] Krüss and Thiele: *Loc. cit.*, p. 72; Gautier and Charpy: *Compt. Rend.*, **111**, 645 (1890); Wiedemann: *Wied. Ann. Phys.*, **269**, 580.

[3] *Compt. Rend.*, **75**, 1511 (1873); *Ann. Chem.* (Liebig), **167**, 86 (1873).

[4] Lachman: *Am. Chem. J.*, **21**, 443 (1899); This Journal, **23**, 897 (1901); Angeli: *Ber. d. chem. Ges.*, **29**, 1884 (1896); Meisenheimer: *Ann. Chem.* (Liebig), **323**, 205 (1902).

iodine solvents, for similar difficulties were met, during this investigation, with amyl bromide and ethylene bromide. The first samples of these substances gave dark red iodine solutions, but after careful purification, pure violet solutions were obtained.

SAN FRANCISCO, September 13, 1902.

[CONTRIBUTIONS FROM THE NEBRASKA EXPERIMENT STATION, NO. I.—SENT BY E. A. BURNETT.]

PRUSSIC ACID IN SORGHUM.

BY HENRY B. SLADE.

Received October 3, 1902.

INSTANCES of the fatal effects of green sorghum upon stock are frequently reported. The Nebraska Experiment Station records 144 fatal cases in a single year. "At Imperial 10 cattle out of a herd of 32 died suddenly. At Culbertson 11 cattle died within an hour from eating cane. At Wauneta a stockman reports the loss of 7 head out of a small herd."[1] From Australia like cases are reported.[2] In one instance 17 animals in a single herd died from eating sorghum; in other instances cattle were allowed to feed upon the cane without loss. Berthelot and André in 1886, in an article on "The Noxious Effects of Sorghum,"[3] ascribed the cause to excessive amounts of potassium nitrate. The late Mr. Williams, of the U. S. Department of Agriculture, also suggested saltpeter as the cause of the trouble.[4] Determinations of the potassium nitrate in poisonous sorghum by Hiltner[5] showed that the amount present was inadequate to the effect produced and the idea was presented that "the plant under certain conditions develops a highly poisonous chemical compound." In a paper before the Nebraska Section of the American Chemical Society[6] the theory was put forward by the writer, in the fall of 1901, that such a poisonous compound might be produced by the action of an enzyme upon a glucoside formed in the plant through a process of abnormal growth.[7] An examination of a sample of sorghum

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[1] Nebraska Experiment Station Bulletin No. 63.

[2] Quoted in Experiment Station Record, **13**, 992.

[3] Abstract in Biedermann's *Centralblatt*, **22**, 470.

[4] Farmers' Bulletin No. 50, p. 17.

[5] Nebraska Experiment Station Bulletin No. 63.

[6] Nebraska Experiment Station, 15th Annual Report, p. 55.

[7] Dunstan and Henry have since confirmed this view in the case of the Great Millet or Sorghum Vulgare of Egypt. Since the above article was contributed the attention of the