

trodialyse. H. R. KRUYT et E. J. W. VERWEY¹⁾ avaient déjà montré que de pareilles impuretés ne se laissent pas éliminer par dialyse prolongée.

IV. *Conclusions.*

1o. La théorie de BUNGENBERG DE JONG se confirme également pour le sol négatif d'iodure d'argent, tout au moins en ce qui concerne les ions tétravalent et hexavalent de thorium et d'hexol. Une partie des ions NO_3 est entraînée notamment par le précipité. Cette partie est toutefois plus faible que pour les sols lyophiles.

L'ion trivalent de cérium au contraire n'est déjà plus en état de provoquer de façon appréciable l'apparition de centres positifs sur le sol de AgI .

2o. Les ions polyvalents, pour produire la floculation du sol, ne passent pas d'une manière quantitative dans la partie fixe de la couche double. La dernière colonne de la table 1 montre qu'il faut chaque fois un grand excès de cation polyvalent, qui reste dans le floculat, pour que la floculation du sol puisse avoir lieu.

3o. En comparant la quantité d'ions d'hydrogène échangée, après floculation par les ions polyvalents, à la quantité totale des ions d'hydrogène déduite des courbes de titrage potentiométriques, nous avons constaté que les ions d'hydrogène ne sont pas échangés de manière quantitative, mais qu'il s'établit un équilibre entre ces ions.

Nos résultats seront publiés in extenso à un autre endroit. Dès maintenant nous ne pouvons manquer d'adresser à Monsieur H. R. KRUYT tous nos remerciements pour l'intérêt qu'il n'a cessé de témoigner pour nos recherches.

Laboratoire de Chimie analytique de l'Université.

Gand, Nov. 1936.

¹⁾ E. J. W. VERWEY et H. R. KRUYT. Zur Kenntnis der elektrischen Doppelschicht bei Kolloiden. IV. Zeits. f. Phys. Chem. Abt. A. **167**, 325 (1934).

Chemistry. — *Further examples of unmixing in aqueous salt solutions.*
By H. G. BUNGENBERG DE JONG and L. TEUNISSEN-VAN ZIJP.
(Communicated by Prof. H. R. KRUYT).

(Communicated at the meeting of October 31, 1936).

In a previous publication¹⁾ examples were given of unmixing in aqueous salt solutions and the significance of these phenomena for the theory of the complex- and auto-complex coacervation was discussed.

¹⁾ H. R. KRUYT and H. G. BUNGENBERG DE JONG, These Proc. **38**, 714 (1935).

Unmixing in aqueous electrolyte solutions is by no means a common phenomenon. In the literature BAKHUIS ROOZEBOOM²⁾ mentions some cases, viz.:

the Cu salt of valerianic acid and caproic acid
Pb-butyrate and Mg-undecylate

These cases are so little stable that they cannot be studied any further; the salts crystallize quickly. A better example is the system water- K-salt of trinitro-oxyphenyl-methylnitramine which has a metastable unmixing-area and of which ROOZEBOOM could make analyses of upper and lower layer.

In the microchemical literature it is often seen that alkaloids unmix with various reagents. A systematic investigation has not yet been made, but we have already found that unmixing sets in when a solution of novocain chloride is mixed with a solution of:

K₃Co(CN)₆
K₃Fe(CN)₆
NH₄-heptamolybdate
Na-picrate
K₂HgI₄

It seems desirable to be acquainted with as many examples as possible in order that we may know in which combinations of two salts unmixing may be expected during the double transmutation. Here we communicate our observations in the combinations:

Na-salt of carboxylic acid + Me-chloride or nitrate where
Me = anorganic cation.

The method of investigation was the same as that described in the previous communication:

On an object-glass are placed side by side a drop of a solution of one of the salts of group A and a drop of a solution of one of the salts of group B. The two drops are then covered with a cover-glass and the contact zone is microscopically examined. If necessary, the preparation is heated for a short while and once more studied microscopically. In this way all mutual combinations of the salts of group A with those of group B have been examined.

From a negative result it should not always be concluded that unmixing is not possible; occasionally the solutions of the organic salts were not stronger than 0.1 N, so that it is not impossible that in higher concentrations the salts may unmix.

²⁾ H. W. BAKHUIS ROOZEBOOM, *Rec. Trav. Chim. des Pays Bas* 8, 257 (1899).

A. Nitrates of Ce, La, UO_2 , Pb, Cu, Cd, Zn, Mn, Co, Ni, Ag;
Chlorides of $\text{Co}(\text{NH})_6$, Mg, Ca, Sr, Ba, Li, Na, K, NH_4 .

B. Sodium salts of:

Valerianic acid, caproic acid, caprylic acid, capric acid;
monochloroacetic acid, trichloroacetic acid;
oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid,
suberic acid, azelaic acid, sebacic acid;
fumaric acid, maleic acid, malic acid, tartaric acid, citric acid, asparaginic
acid;
diethylbarbituric acid;
benzoic acid and its derivatives: p-F, p-Cl, p-Br, p-I, o-oxy, p-oxy,
p-amido, p-methoxy-benzoic acids;
phenylacetic acid, phenylpropionic acid, mandelic acid, cinnamic acid;
phthalic acid, terephthalic acid;
phenolsulphonic acid, α -naphthalinsulphonic acid, β -naphthalinsulphonic
acid, naphtholdisulphonic acid.

In the following table the combinations have been recorded in which
unmixing occurs with certainty. In many of these cases the liquid state of
the precipitate cannot be stated for certain at room-temperature, but only
becomes apparent on heating.

| | | |
|----------------|---|---|
| Na valerianate | + $\text{Pb}(\text{NO}_3)_2$ | : large drops |
| „ | + $\text{Zn}(\text{NO}_3)_2$ | : drops and crystals |
| Na caproate | + $\text{Ce}(\text{NO}_3)_2$ | : drops on heating |
| „ | + $\text{UO}_2(\text{NO}_3)_2$ | : „ „ |
| „ | + $\text{Pb}(\text{NO}_3)_2$ | : „ „ |
| Na caprylate | + $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ | : small drops |
| „ | + $\text{UO}_2(\text{NO}_3)_2$ | : drops |
| „ | + $\text{Cd}(\text{NO}_3)_2$ | : „ |
| „ | + $\text{Mn}(\text{NO}_3)_2$ | : „ |
| „ | + $\text{Co}(\text{NO}_3)_2$ | : „ on heating |
| „ | + $\text{Ni}(\text{NO}_3)_2$ | : „ „ |
| Na caprate | + $\text{UO}_2(\text{NO}_3)_2$ | : „ in the cold |
| Na succinate | + $\text{Pb}(\text{NO}_3)_2$ | : particularly in the heat very beautiful |
| Na glutarate | + $\text{UO}_2(\text{NO}_3)_2$ | : drops on heating |
| „ | + $\text{Pb}(\text{NO}_3)_2$ | : „ in the cold |
| Na adipate | + $\text{Pb}(\text{NO}_3)_2$ | : unmixing |
| Na sebacate | + $\text{UO}_2(\text{NO}_3)_2$ | : on heating very beautiful unmixing |
| Na malate | + $\text{Pb}(\text{NO}_3)_2$ | : on heating |
| „ | + $\text{Cd}(\text{NO}_3)_2$ | : „ beautiful |
| Na tartrate | + $\text{Cd}(\text{NO}_3)_2$ | : „ „ |

| | | |
|--------------------------|---|------------------------------|
| Na asparaginate | + Pb(NO ₃) ₂ | : beautiful unmixing |
| „ | + UO ₂ (NO ₃) ₂ | : in the heat liquid |
| Na benzoate | + Cd(NO ₃) ₂ | : in the heat very beautiful |
| Na salt of p-toluic acid | + Pb(NO ₃) ₂ | : on heating, not beautiful |
| „ | o- „ „ + Pb(NO ₃) ₂ | : „ „ |
| „ phenylacetic | „ + UO ₂ (NO ₃) ₂ | : „ „ |
| „ | „ „ + Cd(NO ₃) ₂ | : beautiful on heating |
| „ phenylpropionic | „ + UO ₂ (NO ₃) ₂ | : unmixing on heating |
| „ | „ „ + Cd(NO ₃) ₂ | : beautiful on heating |

In the 800 examined combinations of the 20 salts of group A with the 40 salts of group B we could only state unmixing with certainty in 29 cases.

The number of cases stated with each of the cations amounted to: Pb⁺⁺ = 9, UO₂⁺ = 8, Cd⁺⁺ = 6, Ce⁺⁺⁺ = 1, Co(NH₃)₆⁺⁺⁺ = 1, Zn⁺⁺ = 1, Mn⁺⁺ = 1, Ni⁺⁺ = 1, Co⁺⁺ = 1.

Evidently in particular the Pb, UO₂ and Cd salts with the Sodium salts of carboxylic acids examined here are in a favourite position with regard to an unmixing at the double transmutation.

Botany. — *Concerning the influence of temperature treatment on the carbohydrate metabolism, the respiration and the morphological development of the tulip.* III. By L. ALGERA. (Communicated by Prof. J. C. SCHOUTE.)

(Communicated at the meeting of October 31, 1936).

DISCUSSION OF THE RESULTS.

The respiration and the carbohydrate metabolism.

Table III and figures 6 and 8 of the preceding publication (1) show that the respiration also after being calculated on the basis of 20° C. is dissimilar in the various lots. Is this to be explained by the assumption that the applied temperature influences the forming or activation of the respiratory enzymes or can the differences discovered be attributed to the difference in the sugar percentage. It has been proved that the concentration of the reducing sugars is little changed by the temperature treatment. It is more obvious to ascertain whether there exists a relationship between the non-reducing sugars and the respiration.