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# PHYSICOCHEMICAL INVESTIGATIONS AND METHODS OF PRODUCING COMPLEX FERTILISERS WITH THE USE OF UREA

G. L. Tudorovskaya and F. G. Margolis

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## I. INTRODUCTION

Urea is a highly concentrated fertiliser containing 46.6% nitrogen, free of inert materials, and is used either independently or in complex fertilisers which contain phosphorus and potassium as well as nitrogen. Furthermore, urea finds use as foodstuff for farm animals, is widely employed in plastics manufacture, in the pharmaceutical industry, and in medicine.

The increase in the demand by agriculture and industry for urea has brought about a considerable increase in the production in the USSR and abroad[1]. The greatest amount of urea is produced in Japan, where 85–90% of the total output is used as a fertiliser, compared with 60–65% in USA, and 20–40% in Europe.

In 1962 urea formed only 8% of the world production of nitrogenous fertilisers; in 1966 [1963 ?] this had grown to 17.5% calculated on nitrogen[2]. The production of urea for industrial purposes is also growing steadily.

In the USSR until recently the use of urea as a fertiliser was quite limited. In 1958 the total fraction of urea in the balance of nitrogenous fertilisers was 1% (calculated on

nitrogen). At the end of 1961 the level of production of the urea in the USSR had increased almost six times in comparison with 1958. In 1962 the USSR occupied third place in the world — after the USA and Japan — as regards output of urea.

According to the latest plan data in the USSR, owing to the improvement in the process the cost per unit of nitrogen in urea exceeds that in ammonium nitrate by 7–15%.[3] With the reduction in the cost of manufacture of urea and the increasing scale of production it is obviously finding wide application in agriculture as a component of fertilisers, both independent and complex.

To choose optimal conditions for carrying out the production of nitrogenous and complex fertilisers employing urea, several equilibrium systems have been studied. This work started in the USSR in the middle of the 'thirties; in recent years there have been further developments.

This article is a review of physicochemical investigations of systems which include urea and compounds containing nitrogen, phosphorus, potassium, and trace elements, and also the commercial methods of preparing fertilisers based on these systems.

## II. PHYSICOCHEMICAL INVESTIGATIONS

### 1. Solubility of Urea in Water and Ammonia

Various investigators have studied the urea–water binary system in detail[4–12]. A summary of the results obtained up to 1935 has been given in a monograph[11]. Soviet investigators subsequently studied the temperature region from complete solidification to 40°.[12–14].

Table 1 gives data on the solution compositions at the cryohydric points and the points of polymorphic transformations.

Various investigators have studied the solubility of urea in liquid ammonia[8,15]. The solubility of urea in liquid ammonia rises considerably with the temperature; starting from ~ 30° the solubility of urea in liquid ammonia exceeds its solubility in water. Urea and ammonia form the compound $CO(NH_2)_2 \cdot NH_3$; it can exist only in solutions containing an excess of ammonia, therefore the solubility curve for urea in liquid ammonia (Fig. 1) has a change in direction at the point $CO(NH_2)_2$ 77.9, $NH_3$ 22.1%, coinciding with the melting point of this compound, 46°.

Fig. 2 shows the $CO(NH_2)_2$–$NH_3$–$H_2O$ system; curves for the vapour pressure over saturated solutions are also given on this diagram.

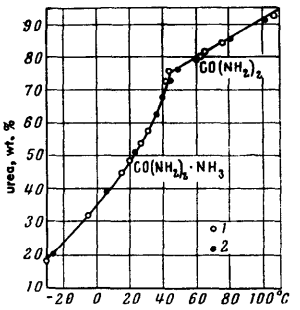



Fig. 1. Solubility curve for urea in liquid ammonia:
1) after Jänecke[8]; 2) after Scholl and Davis[15].

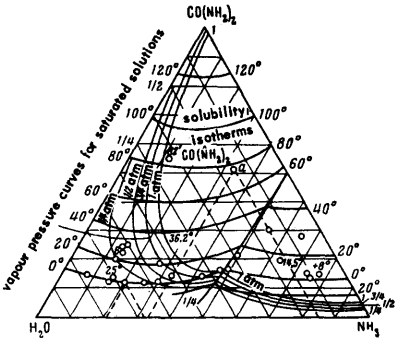



Fig. 2. Equilibrium diagram of the $CO(NH_2)_2$–$NH_3$–$H_2O$ system[8].

TABLE 1.

| Solution composition at cryohydric point, wt. % | | t, °C | Solution composition at first inflection, wt. % | | t, °C | Solution composition at second inflection, wt. % | | t, °C | References |
|---|---|---|---|---|---|---|---|---|---|
| $CO(NH_2)_2$ | $H_2O$ | | $CO(NH_2)_2$ | $H_2O$ | | $CO(NH_2)_2$ | $H_2O$ | | |
| 33.0 | 67.0 | −10.8 | — | — | — | 53.3 | 46.7 | 22.5 | 12 |
| 32.9 | 67.1 | −10.9 | 40.7 | 59.3 | +1.1 | 57.2 | 43.8 | 29.2 | 13 |
| 32.9 | 67.1 | −11.0 | 40.7 | 59.3 | +1.1 | 54.5 | 45.5 | 24.4 | 14 |

### 2. Systems Containing Urea and Nitrates

The $CO(NH_2)_2$–$NH_4NO_3$ anhydrous binary system has been studied by various authors[16,17]. Double compounds are not formed between the components; the eutectic point is at $NH_4NO_3$ 53.5%, 44.6°.[16] Soviet investigators have studied the viscosity and electrical conductivity of this system[18].

The $CO(NH_2)_2$–$NH_4NO_3$–$H_2O$ ternary system has been studied by the visual-polythermal method from 25° to complete solidification (-26.5°)[19] and by the isothermal method at 25°.[20] The polytherm (Fig. 3) is divided into seven crystallisation fields; in addition to the ice field there are three fields each for the polymorphic modifications of urea and ammonium nitrate. The existence of two series of solid solutions in the system has been suggested: urea in ammonium nitrate and ammonium nitrate in urea[19], but in the investigation of this system by the isothermal method solid solutions were not observed in the residues[20].

The electrical conductivity and viscosity of this system at 30° have also been studied[21]. The extrema on the curves in Figs. 4 and 5 are evidence of the formation of the complexes $NH_4NO_3 \cdot CO(NH_2)_2$ and $NH_4NO_3 \cdot 2CO(NH_2)_2$ in the solutions.

The common solubility in the $CO(NH_2)_2$–$NH_4NO_3$–$NH_3$–$H_2O$ system[22] was studied at 30° and 0° and various $NH_3$ : : ($NH_3$ + $H_2O$) ratios. The highest total solubility of the

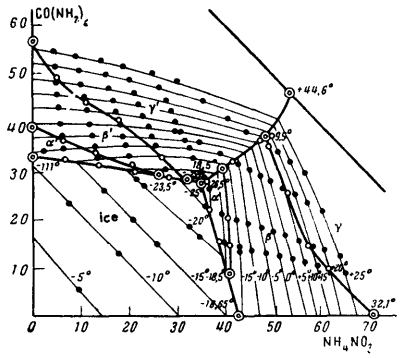



Fig. 3. Polythermal solubility diagram of the $CO(NH_2)_2$–$NH_4NO_3$–$H_2O$ system.

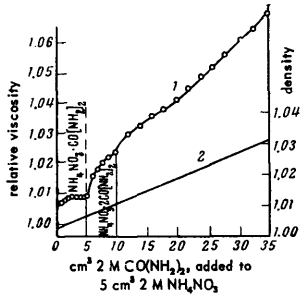



Fig. 4. Viscosity and density curves for the $CO(NH_2)_2$–$NH_4NO_3$–$H_2O$ system at 30°: 1) relative viscosity; 2) density.

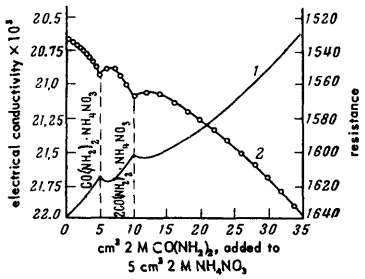



Fig. 5. Electrical conductivity curves for the $CO(NH_2)_2$–$NH_4NO_3$–$H_2O$ system at 30°: 1) electrical conductivity; 2) resistance.

salts at 30° — for 70% $NH_4OH$ and $NH_3$ : ($NH_3$ + $H_2O$) 0.7 — is 96.9%, of which 53.4% comes from the ammonium nitrate.

A complex of urea with ammonia starts to form at 0° and $NH_3$ : ($NH_3$ + $H_2O$) ratios of 0.4–0.5. At the ratio 0.4 the solid phase corresponds to the composition $NH_4NO_3$. $.CO(NH_2)_2$. $0.11NH_3$, at the ratio 0.5 to $NH_4NO_3.CO(NH_2)_2$. $.0.25NH_3$. It is suggested that as the $NH_3$ : ($NH_3$ + $H_2O$) ratio is increased the values of $n$ in the complex formed $CO(NH_2)_2.nNH_3$ will tend to unity.

The solubility of the salts at 30° increases with the $NH_3$ : ($NH_3$ + $H_2O$) ratio. At 0° such a relationship is not observed, owing to the formation of complexes.

On the basis of these results on the mutual solubility the authors [22] recommend for agricultural use a series of ammonia addition compounds, of composition given in Table 2.

Double compounds were not observed in a study of the $CO(NH_2)_2$–$NaNO_3$ anhydrous system [23]. The eutectic point is at $NaNO_3$ 29.5%, 83.9°.

The $CO(NH_2)_2$–$NH_4NO_3$–$NaNO_3$ ternary anhydrous system has been studied [23]. The ternary eutectic point is at $CO(NH_2)_2$ 45, $NH_4NO_3$ 47.5, $NaNO_3$ 7.59%, 37.1°.

The $NaNO_3$–$CO(NH_2)_2$–$H_2O$ three-component system was studied by the visual-polythermal method at temperatures from 40° to complete solidification (-19.55°). [24,25] The formation of an incongruently soluble compound $NaNO_3.CO(NH_2)_2$. $.pH_2O$ was reported [25]. There are six crystallisation fields on the diagram (Fig. 6): ice, three fields of urea ($\alpha$, $\beta$, and $\gamma$ modifications), sodium nitrate, and the compound $NaNO_3.nCO(NH_2)_2.pH_2O$.

It was found that in the $CO(NH_2)_2$–$KNO_3$ binary system the eutectic point is at $CO(NH_2)_2$ 75.7, $KNO_3$ 24.3%, 110°. [26]

Fusion in the $CO(NH_2)_2$–$NH_4NO_3$–$KNO_3$ ternary system was also studied [26]. On the projection of crystallisation surface there is the field of the compound $2NH_4NO_3.KNO_3$, which melts incongruently at 170°. This field narrows to a transformation point at $CO(NH_2)_2$ 48, $NH_4NO_3$ 47, $KNO_3$ 5%, 66°. The ternary eutectic point is at $CO(NH_2)_2$ 44.3, $NH_4NO_3$ 49.9, $KNO_3$ 5.7%, 43° (Fig. 7).

TABLE 2.

| Chemical composition of ammines | | | | | | (NH₃ + H₂O) vapour pressure, mmHg, at | | | | Temperature of deposition of solid phase, °C |
|---|---|---|---|---|---|---|---|---|---|---|
| $NH_4NO_3$, % | $CO(NH_2)_2$, % | $NH_3$, % | $H_2O$, % | total N, % | organic N, % | 10° | 20° | 30° | 40° | |
| 45.1 | 15.2 | 20.1 | 19.6 | 39.41 | 7.09 | 550 | 708 | 917 | 1240 | —32.1 |
| 40.1 | 15.1 | 22.6 | 22.2 | 39.68 | 7.04 | 576 | 756 | 1034 | 1420 | —36.2 |
| 40.3 | 20.0 | 20.1 | 19.6 | 39.97 | 9.33 | 529 | 703 | 957 | 1310 | —29.6 |
| 50.0 | 10.0 | 20.1 | 19.6 | 38.71 | 4.66 | 453 | 616 | 108 | 1130 | —28.3 |

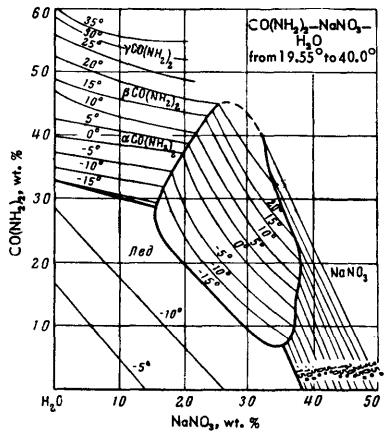



Fig. 6. Polythermal solubility diagram of the $CO(NH_2)_2$–$NaNO_3$–$H_2O$ system.

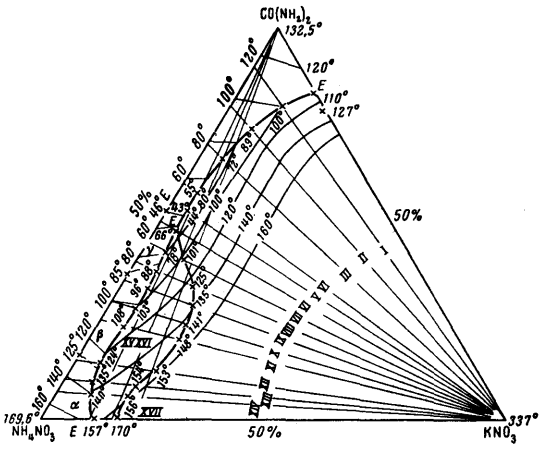



Fig. 7. Equilibrium diagram of the $CO(NH_2)_2$–$NH_4NO_3$–$KNO_3$ system.

Solubility in the $CO(NH_2)_2$–$KNO_3$–$H_2O$ system has been studied by several investigators [27,28]. Fig. 8 shows the diagram of the polytherms of this ternary system [27]; the investigation was by the visual-polythermal method, from 30° to complete solidification. Table 3 gives the compositions corresponding to the eutectic points according to the results of the different investigators.

Fig. 9 shows the 25° isotherm [29] of the $Ca(NO_3)_2$–$CO(NH_2)_2$–$H_2O$ system and the data for the system are also given in Table 4.

The compound $Ca(NO_3)_2.4CO(NH_2)_2$ was first isolated in 1918 by Bosch. A fertiliser of this composition is produced abroad; it has good physical properties, its hygroscopicity being less than that of calcium nitrate.

TABLE 3. Eutectic points in the $CO(NH_2)_2$–$KNO_3$–$H_2O$ system.

| Solution composition, wt. % | | | Temperature, °C | Reference |
|---|---|---|---|---|
| $CO(NH_2)_2$ | $KNO_3$ | $H_2O$ | | |
| 32.2 | 7.8 | 59.0 | −15 | 27 |
| 31.6 | 5.5 | 62.9 | −13.4 | 28 |

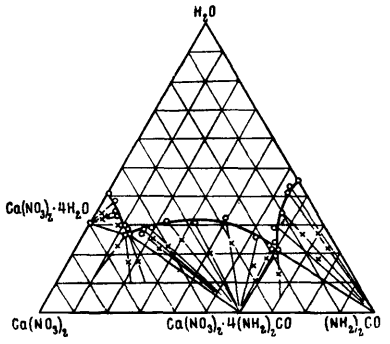



Fig. 9. Isothermal solubility diagram of the $Ca(NO_3)_2$–$CO(NH_2)_2$–$H_2O$ system at 25°.

TABLE 4. Invariant points in the $Ca(NO_3)_2$–$CO(NH_2)_2$–$H_2O$ system at 25°.

| Point No. | Liquid phase composition, wt. % | | | Solid phase |
|---|---|---|---|---|
| | $Ca(NO_3)_2$ | $CO(NH_2)_2$ | $H_2O$ | |
| 1 | 18.19 | 60.52 | 21.29 | $CO(NH_2)_2$—$Ca(NO_3)_2.4CO(NH_2)_2$ |
| 2 | 60.18 | 12.14 | 27.55 | $Ca(NO_3)_2.4H_2O$—$Ca(NO_3)_2.4CO(NH_2)_2$ |

## 3. Systems Containing Urea and Phosphates

Several papers describe the study of the common solubility of urea and various phosphates. The $CO(NH_2)_2$–$H_3PO_4$–$H_2O$ system was studied by the visual-polythermal and isothermal methods [11,30–32]. However, the information given by various authors on the presence of compounds in this system is contradictory. Matignon and Dodé [30] found the compound $CO(NH_2)_2.H_3PO_4$ and the compound $3CO(NH_2)_2.2H_3PO_4$ has been reported [11]. When solubility in this system was studied by the visual-polythermal method three crystallisation fields were observed: ice, urea, and solid solutions of the type $mCO(NH_2)_2.nH_3PO_4$. [31]

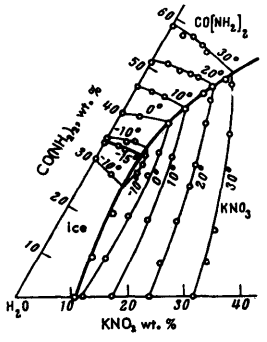



Fig. 8. Polythermal solubility diagram of the $CO(NH_2)_2$–$KNO_3$–$H_2O$ system.

According to recent information, in an isothermal study of solubility at 20° and 40° only urea, uronium phosphate, and their mixtures were observed in the solid phase [32]. Uronium phosphate dissolves congruently (Fig. 10).

The ammonium dihydrogen phosphate–urea–water system has been studied by the visual-polythermal method between −15.3° and 40° [33–35] and by the isothermal method at 25°. [20] It has one ternary point; chemical reaction between the components is not observed (Fig. 11). The cryohydric point is at $CO(NH_2)_2$ 28.8, $NH_4H_2PO_4$ 11.9, $H_2O$ 59.3%, −15.3°.

Solubility in the $(NH_4)_2HPO_4$–$CO(NH_2)_2$–$H_2O$ system was studied at temperatures from −16.6° to 30°. [14] The presence of the crystal hydrate of diammonium hydrogen phosphate $3(NH_4)_2HPO_4.2H_2O$ was confirmed (Fig. 12). Table 5 gives the invariant ternary points in this system.

The same work [14] gives the equilibrium diagram of the $CO(NH_2)_2$–$(NH_4)_2HPO_4$ system. The eutectic is at $CO(NH_2)_2$ 96.3, $(NH_4)_2HPO_4$ 3.7%, 126.7°.

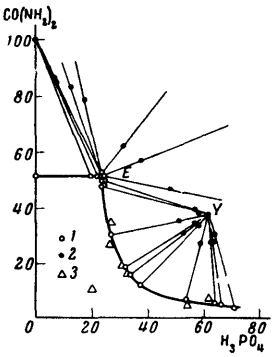



Fig. 10. Isothermal solubility diagram for the $CO(NH_2)_2$–$H_3PO_4$–$H_2O$ system at 20°. Phase compositions: 1) liquid; 2) solid; 3) liquid, calculated from the results of Blidin and coworkers[31]. *E* = uronium phosphate + urea. *Y* = uronium phosphate.

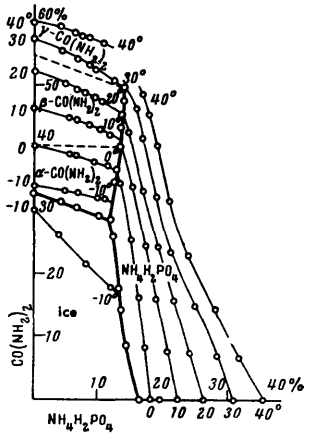



Fig. 11. Polythermal solubility diagram of the $CO(NH_2)_2$–$NH_4H_2PO_4$–$H_2O$ system.

TABLE 5. Invariant ternary points in the $(NH_4)_2HPO_4$–$CO(NH_2)_2$–$H_2O$ system.

| Point No. | Wt. % $CO(NH_2)_2$ | Wt. % $(NH_4)_2HPO_4$ | Wt. % $H_2O$ | per 100 moles dry salts: moles $CO(NH_2)_2$ | per 100 moles dry salts: moles $(NH_4)_2HPO_4$ | Crystallisation temperature, °C | Solid phase |
|---|---|---|---|---|---|---|---|
| 1 | 25.4 | 12.3 | 62.30 | 81.96 | 18.02 | —17.0 | ice + urea + $(NH_4)_2HPO_4.2H_2O$ |
| 2 | 26.7 | 15.90 | 57.4 | 79.87 | 20—13 | —16.2 | urea + $(NH_4)_2HPO_4$ + $(NH_4)_2HPO_4.2H_2O$ |

Solubility in the $KH_2PO_4$–$CO(NH_2)_2$–$H_2O$ system was studied by the visual-polythermal method from 35° to the temperature of complete solidification (-12.9°) [12] (Fig. 13). As the amount of potassium dihydrogen phosphate added is increased the temperature at the transformation point of one modification of urea into another falls from 22.5° to 1°. Evidently there is a region of restricted solid solutions of urea in $KH_2PO_4$ and the formation of compounds between the components is not observed.

## 4. Systems Containing Urea and Sulphates

Solubility in the $CO(NH_2)_2$–$(NH_4)_2SO_4$–$H_2O$ ternary system has been studied from -29° to 40°.[14] The polytherm diagram has six crystallisation fields: ice, solid solutions, the $\alpha$, $\beta$, and $\gamma$ modifications of urea, and the $(NH_4)_2SO_4$. There is one ternary point, at $CO(NH_2)_2$ 20, $(NH_4)_2SO_4$ 32, $H_2O$ 48%, -29°. Along its boundary with the urea field the solid solutions field stretches up to the eutectic of the $CO(NH_2)_2$–$H_2O$ binary system. As the temperature is raised the solid solutions field narrows and shifts to the urea side (Fig. 14).

The solubility of the $K_2SO_4$–$CO(NH_2)_2$–$H_2O$ system was studied by the visual-polythermal method from 25° to the temperature of complete solidification (-13°).[36] The presence of potassium sulphate in the solution has little effect

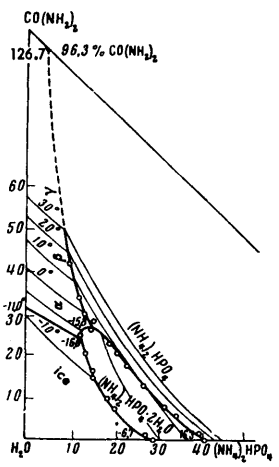



Fig. 12. Polythermal solubility diagram of the $(NH_4)_2HPO_4$–$CO(NH_2)_2$–$H_2O$ system.

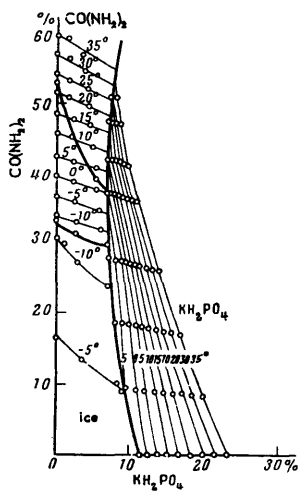



Fig. 13. Polythermal solubility diagram of the $KH_2PO_4$–$CO(NH_2)_2$–$H_2O$ system.

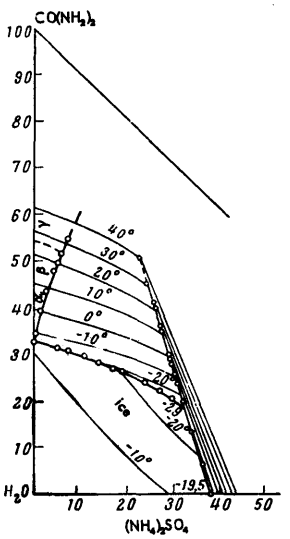



Fig. 14. Polythermal solubility diagram of the $CO(NH_2)_2$–$(NH_4)_2SO_4$–$H_2O$ system.

on the change in solubility of the urea. The ternary eutectic is at $CO(NH_2)_2$ 31.2, $K_2SO_4$ 4.9%, -13°.

The $CaSO_4$–$CO(NH_2)_2$–$H_2O$ ternary system was studied by the isothermal method[37–39] at 0°, 20°, 25°, 40°, and 70°. The compound $CaSO_4 \cdot 4CO(NH_2)_2$ is formed in the system (Fig. 15), and was first studied by Wittaker and coworkers[40].

Solubility in the $MgSO_4$–$CO(NH_2)_2$–$H_2O$ ternary system has been studied by the isothermal and visual-polythermal methods[41–45]. The complex $MgSO_4 \cdot 4CO(NH_2)_2 \cdot H_2O$ exists between 5° and 26° and decomposes at lower temperatures with liberation of urea, and at higher temperatures is converted into $MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$ (Fig. 16). The lower the temperature, the less the influence of urea on the solubility of magnesium sulphate.

## 5. Systems Containing Urea, Chlorides, and Other Compounds.

The KCl–$CO(NH_2)_2$–$H_2O$ system has been studied by several investigators[13,46,47] from -19.4° to 40°. There is no chemical interaction between the components of the

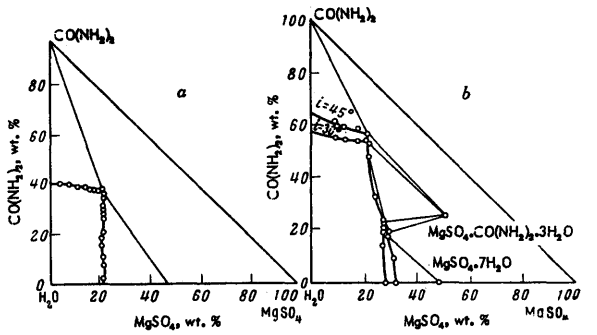



Fig. 16. Isothermal solubility diagrams of the $CO(NH_2)_2$–$MgSO_4$–$H_2O$ system: *a*) 0° isotherm; *b*) 30° and 45° isotherms.

system. The solubility of urea decreases in the presence of KCl. The ternary point of the system is at KCl 13.45, $CO(NH_2)_2$ 26.5%, -19.4°.

Solubility in the KOH–$CO(NH_2)_2$–$H_2O$ system has been studied[48]. Two solubility isotherms (0° and 30°) have been given. At 30° the isotherm has three parts, with the solid phases: $KOH \cdot H_2O$, $KOH \cdot 2H_2O$, and $CO(NH_2)_2$ (Fig. 17).

Several multicomponent systems have been studied to choose optimal conditions for the production of complex fertilisers. The $CO(NH_2)_2$–$NH_4NO_3$–$NH_4H_2PO_4$–$H_2O$ system was studied by the visual-polythermal method from -7° to 50° with $NH_4H_2PO_4$ : $NH_4NO_3$ weight ratios from 0.5 to 4 and total concentrations in the saturated solution of 30, 35, 37, and 40%,[49] and by the isothermal method at 25° and 50°.[20] The composition of the eutonic solution at 25° is: $CO(NH_2)_2$ 40.07, $NH_4NO_3$ 49.03, $NH_4H_2PO_4$ 0.78%.[20] The kinetics of the decomposition of urea in solutions in the presence of ammonium dihydrogen phosphate has been studied[20] at 50°. The 0° solubility isotherm in the $H_3PO_4$–$NH_3$–$CO(NH_2)_2$–KCl–$H_2O$ system has been studied[50]. In pursuing practical objectives, the authors studied restricted regions of this system in accordance with the agricultural requirements for the ratio $N : P_2O_5 : K_2O$ in liquid complex fertilisers. In addition, compositions of solutions for the molar ratios $NH_3 : H_3PO_4$ 1.7, 1.6, and 1.5. A linear relation was also found between the concentration of the total nutrients in solution and the temperature of crystallisation of the solid phase with which this solution is in equilibrium (Fig. 18).

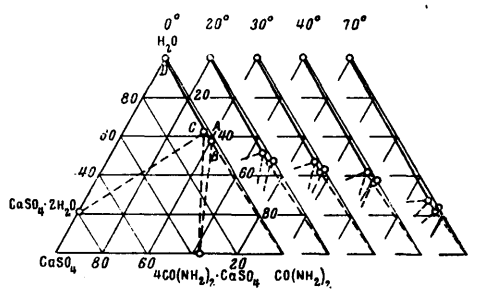



Fig. 15. Isothermal solubility diagrams of the $CaSO_4$–$CO(NH_2)_2$–$H_2O$ system (g per 100 g solution).

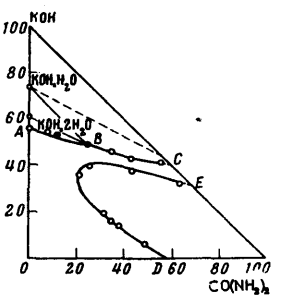



Fig. 17. Isothermal solubility diagram of the KOH–$CO(NH_2)_2$–$H_2O$ system at 30°.

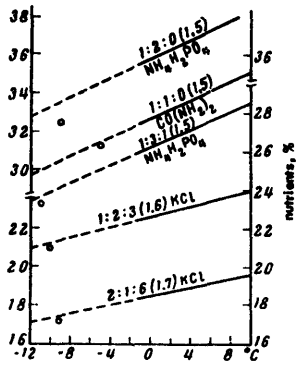



Fig. 18. Circles: measured values. Broken lines: extrapolated values. In parentheses: $NH_3:H_3PO_4$ molar values.

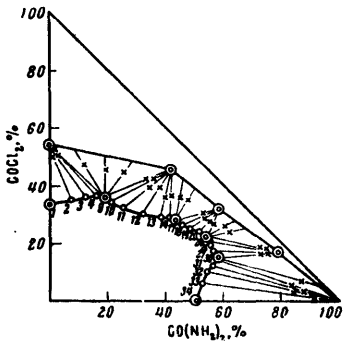



Fig. 20. Isothermal solubility diagram of the $CoCl_2-CO(NH_2)_2-H_2O$ system at 20°.

Solubility in the $CO(NH_2)_2-NH_4NO_3-NH_3-H_3PO_4-KCl-H_2O$ system at 0° was also studied only for selected ratios of the nutrients[50]. Fig. 19 gives a diagram of this system at 0°.

## 6. Systems Containing Urea and Trace Elements

In recent years several systems containing urea and compounds used as sources of trace elements (boron, manganese, copper, zinc, cobalt, etc.) have been investigated.

Mutual solubility in the $CoCl_2-CO(NH_2)_2-H_2O$ system at 20° has been studied[51] (Fig. 20, Table 6).

The 30° solubility isotherm of the $CoSO_4-CO(NH_2)_2-H_2O$ system[42,43] consists of four branches. Two complexes of cobalt and urea are formed in this system: $CoSO_4.2CO(NH_2)_2.4H_2O$ and $CoSO_4.6CO(NH_2)_2$ (Fig. 21).

In studying solubility in the $NiSO_4-CO(NH_2)_2-H_2O$ system[52] compounds analogous to those formed by urea with cobalt sulphate were found: $2CO(NH_2)_2.NiSO_4.4H_2O$ and $6CO(NH_2)_2.NiSO_4$. The system was studied at 25° and 40°.

TABLE 6. Invariant points of the $CoCl_2-CO(NH_2)_2-H_2O$ system.

| Composition of the solution, wt. % | | | Composition of the solid residues, wt. % | | Solid phase |
|---|---|---|---|---|---|
| $CoCl_2$ | $CO(NH_2)_2$ | $H_2O$ | $CoCl_2$ | $CO(NH_2)_2$ | |
| 33.79 | — | 66.21 | 50.64 | — | $CoCl_2-6H_2O$ |
| 36.01 | 19.87 | 44.62 | 47.72 | 11.67 | $CoCl_2\cdot6H_2O+CoCl_2\cdot2(NH_2)_2CO\cdot2H_2O$ |
| 28.28 | 43.19 | 28.53 | 36.15 | 45.13 | $CoCl_2\cdot2(NH_2)_2CO\cdot2H_2O+CoCl_2\cdot4(NH_2)_2CO\cdot2H_2O$ |
| 23.03 | 54.62 | 22.35 | 25.70 | 60.64 | $CoCl_2\cdot4(NH_2)_2CO\cdot2H_2O+CoCl_2\cdot10(NH_2)_2CO\cdot2H_2O$ |
| — | 51.15 | 48.85 | — | 95.63 | $Co(NH_2)_2$ |

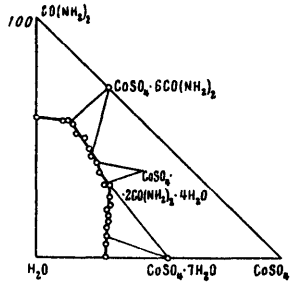



Fig. 21. Isothermal solubility diagram of the $CoSO_4-CO(NH_2)_2-H_2O$ system at 30°.

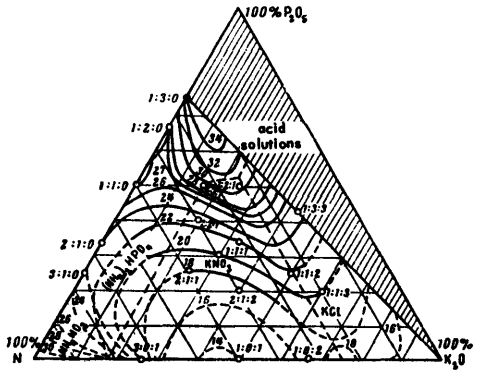



Fig. 19. Isothermal solubility diagram of the $CO(NH_2)_2-NH_4NO_3-H_3PO_4-NH_3-KCl-H_2O$ system at 0°.

The solubility of zinc sulphate in the presence of urea was studied by the visual-polythermal method at temperatures from -20.4° (the temperature of complete solidification) to 25°.[53] The ternary eutectic point is at $ZnSO_4$ 25.4, $CO(NH_2)_2$ 26.2, $H_2O$ 48.4%. Formation of complexes was not observed.

Solubility in the $CuSO_4-CO(NH_2)_2-H_2O$ system was also studied by the visual-polythermal method[42] from -18.4° to 30°. The solutions are viscous. The system tends to give supersaturated and supercooled solutions. The solubility of copper(II) sulphate rises from 12.5% at the eutectic point of the $CuSO_4-H_2O$ binary system to 23% at the ternary eutectic point, which suggests chemical reaction between the components. The concentrations of urea in solutions corresponding to the eutectic points of the binary and ternary systems are almost the same. The ternary eutectic

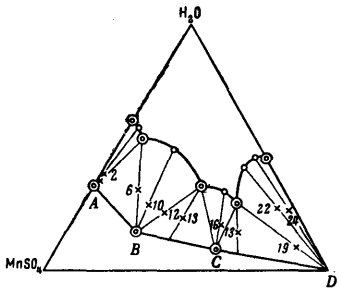



Fig.22. Isothermal solubility diagram of the $MnSO_4$–$CO(NH_2)_2$–$H_2O$ system at 20°: *A*) $MnSO_4.4H_2O$; *B*) $MnSO_4.CO(NH_2)_2.2H_2O$; *C*) $MnSO_4.4CO(NH_2)_2.2H_2O$; *D*) $CO(NH_2)_2$.

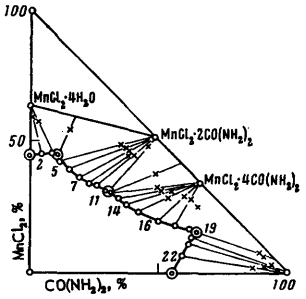



Fig.23. Isothermal solubility diagram of the $CO(NH_2)_2$–$MnCl_2$–$H_2O$ system at 30°.

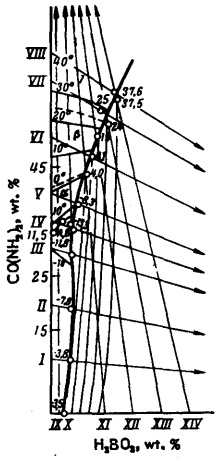



Fig.24. Polythermal solubility diagram of the $H_3BO_3$–$CO(NH_2)_2$–$H_2O$ system.

point is at $CO(NH_2)_2$ 32, $CuSO_4$ 23, $H_2O$ 45%, -18.4°. It has been suggested that two complexes of urea and copper(II) sulphate may be formed, by analogy with cobalt sulphate, in the liquid phase, but complexes have not been observed in the solid phase.

Solubility has been studied [54-56] in the $MnSO_4$–$CO(NH_2)_2$–$H_2O$ system at 10°, 20°, and 25° (Fig. 22).

The solubility in the $MnCl_2$–$CO(NH_2)_2$–$H_2O$ system was studied at 20° and 30° [57] and the specific gravity and viscosity of the equilibrium solutions were measured. Two compounds $MnCl_2.2CO(NH_2)_2.H_2O$ and $MnCl_2.4CO(NH_2)_2$ crystallise at 20° in addition to the two components, and the compounds $MnCl_2.2CO(NH_2)_2$ and $MnCl_2.4CO(NH_2)_2$ at 30° (Fig. 23).

Mutual solubility of the components in the $H_3BO_3$–$CO(NH_2)_2$–$H_2O$ system has been studied at temperatures from -14° (the temperature of complete solidification) to 50°. [58] Formation of compounds was not observed. The ternary eutectic point is at $H_3BO_3$ 3.7, $CO(NH_2)_2$ 36.5, $H_2O$ 59.8%, -14°. The polytherm of the ternary system is divided into three branches: ice, urea, and boric acid. The solubility of urea is almost unchanged in the presence of boric acid, but the solubility of boric acid rises slightly in the presence of urea (Fig. 24).

## III. TECHNOLOGY OF THE PRODUCTION OF COMPLEX FERTILISERS WITH USE OF UREA

The results of the physicochemical investigations were used to choose optimal conditions for various processes for the production of urea-containing fertilisers. Thus the production of the nitrogenous fertiliser, known on the world market under the trade name of "Calurea", is based on the production of a complex of urea and calcium nitrate. The ratio of the components in the compound corresponds to the formula $Ca(NO_3)_2.4CO(NH_2)_2$. This fertiliser displays better physicochemical properties than each of its constituents, that is, lower hygroscopicity and less deterioration on storage. When the calcium nitrate in this fertiliser is in excess then the mixture exhibits a greater hygroscopicity than calcium nitrate alone. The fertiliser is made by dissolving accurately measured quantities of urea in hot concentrated solutions of calcium nitrate (specific gravity 65° Bé) at 80–100°. The compound $Ca(NO_3)_2.4CO(NH_2)_2$ crystallises out on cooling [11]. Many patents have proposed different methods for obtaining fertilisers including $Ca(NO_3)_2.4CO(NH_2)_2$. [11,59-62] The mixtures can include salts of magnesium, calcium, and other metals. Fertilisers have also been patented in which urea is combined with calcium or magnesium basic nitrate, for example $Ca(OH)NO_3.2CO(NH_2)_2$. [63]

The existence of the compound $Ca(NO_3)_2.CO(NH_2)_2.3H_2O$ has been established. In comparison with "Calurea" it contains less urea and is readily granulated [64]. Urea is known to form solid solutions with some fertilising salts (for example, with ammonium sulphate, potassium phosphate, etc.) [12,14].

Several methods for preparing fertilisers containing urea and ammonium sulphate have been proposed [65,66]. Urea is dissolved in sulphuric acid at 80–1000° and the mixture neutralised with an excess of ammonia. Owing to the heat of reaction most of the water is vaporised. Then the mixture is dried and ground [65].

Mixed crystals of urea and $KNH_4HPO_4$ have been suggested for use as a fertiliser [67].

The widest use of urea is in the production of mixed fertilisers, which are composed of simple or double superphosphate, potassium salts, and other compounds. Urea is employed in these fertilisers predominantly as its ammines, often mixed with ammonium nitrate for the ammoniation of superphosphates [68-73].

Urea ammines cause hardly any corrosion of equipment made of ordinary steel.

Solutions obtained at one of the stages in the production of urea — at the exit of the synthesis column or after distillation — have also been suggested for use in the ammoniation of superphosphate. The fertiliser contains about 3.65% N, and 16.3% $P_2O_5$.[70]

Jensen has described[71] a process for the production of complex fertilisers containing urea. The experiments were made on a semi-plant apparatus using a TVA-type† ammoniator–granulator and a horizontal rotating drying drum. Urea ammines were used for the ammoniating solution and simple or double superphosphates and potassium chloride were employed. The author notes that no special difficulties were experienced in granulating complex fertilisers with $N:P_2O_5:K_2O$ ratios of 8:16:16, 10:10:10, or 5:20:20. The duration of the material in the granulator was 10 min, and the temperature of the product at entry 66–93°. It was in the drying drum for 15 min, and the temperature of the product on leaving was 66–121°. The hydrolysis of the urea was negligible.

Phillips[72] studied the conditions for granulating complex fertilisers containing simple or double superphosphate, potassium chloride, ammonium sulphate, etc. in an apparatus similar to that described. Ammoniating solutions of two compositions were used: ammines of ammonium nitrate and urea and ammonium nitrate ammine alone. It was noted that granulation proceeds best in working with solutions containing both ammonium nitrate and urea.

Jewell[74] studied, under laboratory conditions, the granulation of complex fertilisers with $N:P_2O_5:K_2O$ = = 10:10:18, obtained from superphosphate made from Moroccan phosphorite, ammonium nitrate or sulphate, urea, and potassium chloride. The amount of urea introduced into the fertiliser was varied from 2 to 15%. A mechanism has been suggested[74] for the hydrolysis of urea during the production and storage of complex fertilisers, depending on their acidity or alkalinity. The effect of moisture, acidity, and urea content on the stability of complex fertilisers has been determined.

The optimal conditions for obtaining and storing fertilisers so as to retain the stability of the product have been found, namely, entry temperature of product in drying $\geqslant$ 70°, reaching 90° during drying for $\geqslant$ 15 min. Temperature of storage of the fertiliser $\geqslant$ 35°, then the loss of nitrogen is negligible.

Several authors[11,73,75,76] note that to obtain fertilisers with good physicochemical properties, urea must be added in limited amounts. Several Japanese patents propose the manufacture of mixed fertilisers based on urea and superphosphate; the superphosphate should be neutralised without fail, for otherwise the urea reacts with the monocalcium phosphate to form uronium phosphate, dicalcium phosphate, and water[77] by the reaction:

$$Ca(H_2PO_4)_2\cdot H_2O+CO(NH_2)_2=H_3PO_4\cdot CO(NH_2)_2+CaHPO_4+H_2O.$$

Because of the presence of water the mixture becomes greasy, and unsuitable for spreading. Dolomite[78], ammonia[79,80], sodium hydrogen carbonate[81] are among the neutralising additions that have been suggested.

† TVA = Tennessee Valley Authority (Ed. of Translation).

When neutralising additions are made, the monocalcium phosphate is partly or completely converted into dicalcium phosphate by the reaction:

$$CaH_2P_2O_8\cdot H_2O+CaCO_3+H_2O=2CaHPO_4\cdot 2H_2O+CO_2,$$

during which the hygroscopic moisture is converted into the water of crystallisation of the dicalcium phosphate. During the reaction of dicalcium phosphate dihydrate with urea, the latter accelerates the loss of the water of crystallisation[77]. Mixtures of dicalcium phosphate and urea exhibit approximately the same hygroscopicity as urea itself, with the exception of the instances when urea is present in small amounts.

Methods have been developed for making complex fertilisers with use of urea based on the products of the sulphuric acid[82–91] and nitric acid[92–102] treatment of phosphate raw materials. Thus, a Japanese patent proposes the addition of urea to a suspension of phosphogypsum in phosphoric acid, obtained by the decomposition of natural phosphate with sulphuric acid. The reaction is carried out at $\geqslant$ 80°. The suspension is then neutralised with ammonia and the product is dried at 70° to give a fertiliser with the composition (%): $CaSO_4.4CO(NH_2)_2$ 77.48, $NH_4H_2PO_4$ 20.86, $H_2O$ 1.9, $CaHPO_4.2H_2O$ traces, $P_2O_5$ 12.35, N 26.32. $N:P_2O_5$ 2.1:1.

Another Japanese patent[84] recommends the treatment of phosphorite with a mixture of sulphuric acid and urea followed by separation of the reaction products. The decomposition proceeds by the equation:

$$Ca_3(PO_4)_2+3H_2SO_4+12CO(NH_2)_2=2H_3PO_4+3[CaSO_4\cdot 4CO(NH_2)_2].$$

The reaction products contain calcium sulphate–4-urea in the precipitate and phosphoric acid and urea in the solution. Sodium alkylbenzenesulphonate is added to the reaction mixture to facilitate filtration. The yield of $H_3PO_4$ is 95%. Calcium sulphate is known to give a double compound with urea $CaSO_4.4CO(NH_2)_2$[40] which exhibits good physical properties. Apparently when urea is added to the product of the decomposition of phosphatic raw materials with sulphuric acid, which contain calcium sulphate, this double salt is formed. The Japanese investigators investigated the conditions for its production and determined its physicochemical constants and solubility in water[39,86–89].

Several patents recommend the use of phosphogypsum, which is a byproduct in the extraction method of making phosphoric acid, for mixing with urea.

Several articles and patents describe the production of urea-containing complex fertilisers based on the decomposition of phosphates with nitric acid. Japanese investigators published the first studies of the chemistry of the process[92,93]. Depending on the ratio between phosphorite, nitric acid, and urea, various reactions can take place, with the formation of calcium phosphates, uronium phosphate, and calcium nitrate–urea double compound.

An investigation of the hygroscopicity of the fertilisers produced showed that the best results are obtained when 1 mole $Ca_3(PO_4)_2$ takes not less than 4 moles conc. nitric acid (60%) and not less then 9 moles urea. The product contains $P_2O_{5\,tot}$ 9, $N_{tot}$ 24–25% (19–20% in the amide form).

Soviet investigators confirmed that the final products are double compounds: calcium nitrate–urea and uronium phosphate[94,95]. It was noted that uronium nitrate is

formed as an intermediate. The following reactions take place:

(1) $Ca(NO_3)_2 \cdot 4H_2O + 2H_3PO_4 \cdot 5H_2O + 2CO(NH_2)_2 = 2CO(NH_2)_2 \cdot HNO_3 + Ca(H_2PO_4)_2 \cdot H_2O + aq$,

(2) $Ca(NO_3)_2 \cdot 4H_2O + 4CO(NH_2)_2 = Ca(NO_3)_2 - 4CO(NH_2)_2$,

(3) $2CO(NH_2)_2 \cdot HNO_3 + Ca(H_2PO_4)_2 \cdot H_2O + 4CO(NH_2)_2 = Ca(NO_3)_2 \cdot 4CO(NH_2)_2 + 2CO(NH_2)_2 \cdot H_3PO_4$.

Some authors propose to neutralise the nitric acid extract with CaO, $Ca(OH)_2$, $CaCO_3$, or ammonia before or after the introduction of urea [96-100]. Others add the urea without neutralisation [93,97,98].

It is recommended to add urea to the product of the decomposition of phosphatic raw materials with strong nitric acid (70%) — nitrosuperphosphate — which contains 6–8% free acid; this prevents the liberation of oxides of nitrogen from the product and facilitates the production of a fertiliser with good physicochemical properties [101,102].

Methods have also been proposed for the production of urea-containing complex fertilisers based on the treatment of phosphates with a mixture of sulphuric and nitric acids [97,103,104]. For example [104], a mixture of 100 g natural phosphate (31.1% $P_2O_5$), 68 g $K_2O$, and 50 g urea is treated with a mixture of 35 g $H_2SO_4$ (98%) and 17.23 g $HNO_3$ (50%). There is 16% excess of acid against the stoichiometric amount. The product is treated with 8 g $MgCO_3$. The fertiliser obtained contains: $P_2O_{5\,tot}$ 7.91, $P_2O_{5\,avail}$ 7.58, $P_2O_{5\,sol}$ 7.5, $N_{nitr}$ 5.43, $N_{urea}$ 5.06, $K_2O$ 8.52%.

A method for making complex fertilisers during urea synthesis has been proposed [105]. Phosphorus pentoxide is used to remove water from the sphere of reaction during the conversion of carbamate into urea and an excess of ammonia is introduced. The reactions are:

$$NH_4CO_2NH_2 = NH_2CONH_2 + H_2O;$$
$$3H_2O + P_2O_5 = H_3PO_4;$$
$$2NH_3 + H_3PO_4 = (NH_4)_2HPO_4;$$

and yield a mixture of urea and diammonium hydrogen phosphate. The introduction of phosphorus pentoxide lowers the temperature for the synthesis of urea, accelerates the process, and increases the yield of urea. It has been found that at 160° the conversion is 53% with respect to the $NH_3$, 48% with respect to the $CO_2$. The fertiliser contains N 31, $P_2O_5$ 33%.

A method for obtaining double concentrated fertilisers using urea and phosphorus pentoxide as raw materials has been patented in the USA. [106] In this method a solution of urea is mixed with $P_2O_5$, the mixture is cooled and ammonia is added, giving a melt containing urea and $NH_4H_2PO_4$; the slab is then granulated. The fertiliser contains N 24, $P_2O_5$ 31%.

A method has been proposed [107] for making highly concentrated fertilisers containing 60–81% nutrients by fusing urea with monocalcium phosphate and potassium metaphosphate. The melting point of the mixture is 122–129°. The fusion of urea, readily soluble $KH_2PO_4$, and $KPO_3$ (sparingly soluble in water) with the introduction into the melt of trace elements enables complex fertilisers to be produced with any combination of soluble and insoluble potassium phosphates and various ratios of nutrients. A disadvantage of the fusion process is the partial decomposition of the urea (2%). [107]

Shell Chemicals is commercially producing a fertiliser made by fusion sulphur with urea and granulating the product; it contains urea 40, sulphur 10%. [108]

In addition to the use of urea as a constituent of complex and complex mixed fertilisers, it (together with ammonia) is a principal source of nitrogen in the manufacture of liquid complex fertilisers. Unlike ammonium nitrate, urea weakly salts out ammonium phosphate, therefore liquid fertilisers based on it have a higher concentration of nutrients — 27%, instead of 15–17% for ammonium nitrate basis (liquid concentrated fertiliser does not crystallise at 0°).

Urea is known to form various polymeric compounds. The polymer with formaldehyde gives under certain conditions a fertiliser with a long-acting form of nitrogen. Such a fertiliser is especially effective on irrigated soils and under conditions of a moist climate. This increases the degree of utilisation of the nitrogen and decreases its loss.

The problems connected with the use of urea in liquid fertilisers and also the composition of the fertilisers which contain slow-acting forms of nitrogen will not be discussed in this article.

From this review it is evident that there have been many physicochemical investigations of systems which include urea and other fertilisers as components. Knowledge of the equilibrium systems allows optimal process conditions to be selected for obtaining urea-containing fertilisers of required composition, whether liquid or solid.


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# FLUORINATED STEROIDS

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When studying methods for introducing an oxygen substituent at position 11 of a steroid molecule, Fried and Sabo[1] in 1954 observed unexpectedly that 9α-fluoro-11β,17α,21-trihydroxypregn-4-ene-3,20-dione has a several times greater hormonal and anti-arthritic activity than has cortisol. This discovery formed the beginning of a new field of research — the synthesis of modified steroidal compounds — in steroid chemistry. The number of papers and patents which have appeared during the past decade on the chemistry and pharmacology of these compounds has already reached thousands. The introduction of additional alkyl groups, heteroatoms, and double bonds into a steroid molecule produces a considerable increase in the hormonal activity of natural steroids. Special interest attaches to fluorinated steroids among modified steroids, since the introduction of fluorine into a steroid molecule produces a great change in the physiological activity of the hormone.

## I. METHODS OF INTRODUCING FLUORINE INTO A STEROID MOLECULE

The synthesis of 9α-fluoro-11β,17α,21-trihydroxypregn-4-ene-3,20-dione was first accomplished by Fried and Sabo[1], who opened the 9β,11β-oxide by means of hydrogen fluoride. Since then the cleavage of oxides has become one of the main methods for introducing fluorine into many positions in the steroid molecule. However, the exceptionally high physiological activity of fluorinated steroids has led investigators to seek new methods for the synthesis of fluorinated steroids. Thus methods have been worked out for introducing fluorine on the basis of the reaction of steroid olefins with an *N*-halogeno-amide and hydrogen fluoride[2] and with lead tetrafluoride[3], the reaction of steroid ketones with sulphur tetrafluoride[4], and of hydroxy-compounds with silver fluoride or hydrogen fluoride and other reagents; perchloryl fluoride has been studied and used for the synthesis of fluorinated steroids[5].

The above methods enable compounds to be prepared having isolated fluorine atoms, as well as *gem*- and *vic*-difluoro-derivatives. By combining several methods it is possible to introduce successively into the steroid molecule two, three, and four fluorine atoms, which produces a marked increase in the physiological activity of the steroids (see Section II).

The scope of the various methods of synthesising fluorinated steroids is summarised in Table 1, from which it is seen that each method has its own specific field of application, seldom overlapping with those of other methods. Therefore the suitability of different processes for introducing fluorine at a given position in the steroid molecule can be compared only in a few cases. Thus the synthesis of 6-fluoro-steroids, for example, can be effected by three methods, based on the addition of fluorine-containing reagents to the 5–6 double bond. When the steroid contains one double bond, synthesis through the 5α,6α-oxides is mostly used. With polyunsaturated steroids the corresponding oxides are obtained unselectively and in very low yields, and it therefore becomes more convenient to apply the addition of mixed halogens. The addition of lead tetrafluoride has the advantage over both these methods that it enables fluoro-derivatives having the 6α configuration to be obtained directly.

### 1. Opening of Steroid Oxides by Fluorine-Containing Reagents

The introduction of a fluorine atom into a steroid molecule by opening an epoxide with hydrogen fluoride, which takes place by an $S_N2$ mechanism and leads to a *trans*-diaxial cleavage of the oxide ring, has become one of the principal methods for introducing a fluorine atom not only into position 9 but also into positions 2, 6, 12, 15, 17, and 20 in the steroid molecule, since the corresponding epoxides are quite accessible and the techniques are simple.

Fluorinating agents which have been used in these cases are, besides hydrogen fluoride, 48% hydrofluoric acid, potassium hydrogen fluoride, and the boron trifluoride–ether