than in the English malt. This speaks volumes for the value of malt analysis when conducted as described above.

NOTE .- Preparation of cold water malt extract. Fifty grams of ground malt are added to 500 cc. cold distilled water, and allowed to stand four hours with frequent stirring. It is then filtered absolutely brilliant, and used as directed.

THE LABORATORY, ALBION BREWERY,

OLDHAM, ENGLAND.

## ON THE REACTION BETWEEN MOLYBDIC ACID AND POTASSIUM CHROMATE AND BICHROMATE.

BY ROBERT H. BRADBURY.

MOLYBDENUM, as its position in the periodic system of the elements would indicate, offers many analogies with sulphur and more particularly with chromium. Thus, the most important acid of each is H<sub>RO</sub>, and the most stable acid-forming oxide RO.. Again, sulphur and chromium have for some time been known to form a higher unstable oxide R<sub>2</sub>O<sub>2</sub>, and more recently a hydrated Mo<sub>2</sub>O<sub>2</sub> has been prepared and investigated.

Potassium bichromate, K<sub>2</sub>Cr<sub>2</sub>O<sub>2</sub>, is more fully written K<sub>2</sub>CrO<sub>4</sub>CrO<sub>3</sub>, that is, it consists of a molecule of the neutral chromate combined with a molecule of chromic anhydride, and still higher anhydrochromates, e. g., potassium trichromate,  $K_{2}Cr_{3}O_{10}$  or  $K_{2}CrO_{2}CrO_{3}$ , have been shown to exist. The marked likeness between molybdenum and chromium led to the supposition that it might perhaps be possible to replace the chromium in potassium bichromate by molybdenum-that is, to obtain a compound K, CrO, MoO, Since the bichromate results by the direct addition of chromic anhydride to the neutral chromate, it was supposed that the hypothetical chromo-molybdate might result by simple addition of molybdic anhydride to potassium chromate, thus

 $K_2CrO_4 + MoO_3 = K_2CrO_4.MoO_3$ .

At the suggestion of Dr. Smith I have investigated this subject, and while the result is not what was expected, it is of interest as adding another to the long list of facts which show that the rôle played by a substance in a reaction depends not only on the special qualities of the substance, but also to an equal degree on the amount in which it is present. The reaction which ensues when molybdic anhydride is brought together with chromates has been investigated : A in the case of potassium chromate, B with potassium bichromate.

A. In determining the reaction of molybdic anhydride with neutral potassium chromate, the salt was dissolved in water and an equivalent quantity of molybdenum trioxide was added in small portions. Whether in the cold or in warm solution the molybdenum trioxide rapidly dissolves, the solution at the same time turning deep yellow red in color. The molybdic oxide dissolves more rapidly when the process is executed in warm solution. The liquid was then slowly evaporated. At first there separated out from the solution a white mass. It was filtered, dried, and examined. It contained no chromium and was chiefly made up of unaltered molybdenum trioxide, perhaps with some potassium molvbdate. The filtrate, which still retained its reddish-vellow tint, was evaporated. Further separation of the white material was constantly observed. From time to time it was again filtered off and the evaporation continued. At length a filtrate was obtained which was small in bulk and which apparently contained no more of the molvbdic acid. In this, the reddish-vellow color which has already been referred to, was much deeper, corresponding with the increased concentration and showing that none of the colored material had been removed by the filtrations. This liquid was evaporated to crystallization and allowed to The mass of red needles which separated was dried and stand. recrystallized. This material was then examined. Under the microscope it did not differ from potassium bichromate, either in crystallization or in behavior toward polarized light. Analysis revealed the presence of but a trace of molvbdemum and allowed no further doubt as to its nature.

The reaction between potassium chromate and molybdic anhydride therefore proceeds in the sense of the following equation:

$$2K_2CrO_4 + MoO_3 = K_2Cr_2O_7 + K_2MoO_4.$$

No direct addition takes place and no chromo-molybdate is produced. It follows from the fact that much unchanged molybdic anhydride separated out during evaporation and that the liquid contained a great deal of unaltered potassium chromate that the reaction is by no means quantitative. In fact the amount of potassium bichromate formed is exceedingly small relatively to the quantities of potassium chromate and molybdic anhydride employed. Indeed we should expect from the position of molybdenum in the periodic system, from its higher atomic weight and from all the properties of its acid that the avidity of molybdic acid would be much less than that of chromic acid and therefore that the reaction

 $_{2}K_{2}CrO_{4} + MoO_{3} = K_{2}Cr_{2}O_{7} + K_{2}MoO_{4}$ 

would not proceed very far before the stage of equilibrium would be reached in which the backward reaction

 $K_{2}Cr_{2}O_{1} + K_{2}MoO_{4} = 2K_{2}CrO_{4} + MoO_{3}$ 

attains the same velocity as the principal one and in which therefore the transformation ceases.

It would be possible, probably, to increase the quantity of potassium bichromate formed by increasing the amount of molybdic anhydride until a large excess of it was present, but no experiments in this direction have been made.

B. When molybdic anhydride is introduced into a solution of potassium bichromate in the cold no change appears to occur, but no experiments beyond a rough test have been carried out in this direction. The reaction which was investigated between potassium bichromate and molybdic acid takes place only at higher temperatures. Equivalent quantities of potassium bichromate and molybdic anhydride were mixed together and heated gently in a porcelain crucible. The mixture melts rather easily to a blackish-brown liquid and at the same time an effervescence, escape of oxygen, is noticed, which becomes more energetic as the temperature is raised. When the fusion became quiet the lamp was removed. On cooling, the contents of the liquid solidified to a brown mass, which was broken up and treated with hot water. Some unchanged bichromate was removed by this procedure and the insoluble residue was thoroughly washed and It is a soft, loose powder of brown color. It was then dried. subjected to analysis.

Hydrochloric acid dissolves most of it to a green solution, giving off chlorine. A small quantity of black residue remains which is not affected by nitric acid, or by nitric acid and potassium chlorate, or by fusion with sodium carbonate and sulphur. On this account this residue was simply dried on a weighed filter and its weight deducted from that of the substance taken.

The process of analysis may be briefly described. The material was weighed out into a beaker, addition of sufficient strong hydrochloric acid to cover it was made and the heat of a water-bath applied. After complete decomposition, the residue, invariably slight in amount, was filtered off on a weighed filter and its weight deducted from that of the substance taken. The green filtrate was largely diluted with water and hydrogen sulphide passed into it for a long period. Molybdic trisulphide (MoS<sub>2</sub>) precipitated. It was filtered on a weighed filter and its weight determined. An aliquot portion of the precipitate was taken and ignited in a Rose crucible in a strong current of dry hydrogen to convert it into molybdenum disulphide, MoS. The heat applied here must not be too high, or part of the material volatilizes vielding a black sublimate and loss of weight is the result. The molvbdenum disulphide was allowed to cool in the current of gas and then weighed, and the quantity of molybde. num corresponding to the whole of the precipitate and therefore to the substance taken was found by the appropriate calculations. From the filtrate the chromium was precipitated as hydroxide by the addition of ammonia and was estimated in the usual way as sesquioxide.

The potassium in the filtrate from the chromium was weighed as usual, as chloride.

The results follow:

|    | Α.                   | В.    | С.    | Mean.         |
|----|----------------------|-------|-------|---------------|
| Mo | 43.69                | 43.56 | 43.17 | 43.45         |
| Cr | 14.71                | 14.65 | 15.00 | 14.79         |
| К  | 11.08                | ••••  | 11.86 | 11.47         |
|    | Oxygen by difference |       |       | 30. <b>29</b> |

The formula K<sub>2</sub>O.Cr<sub>2</sub>O<sub>3</sub>.3MoO<sub>3</sub> requires the following composition:

| Mo | 42.42 |
|----|-------|
| Cr | 15.44 |
| К  |       |
| 0  | 30.63 |

The compound in question is thus a basic molybdate of chromium and potassium.

UNIVERSITY OF PENNSYLVANIA, June, 1894.