

A NEW ABSOLUTE METHOD OF HYGROMETRY

II. THE PROPERTIES OF POTASSIUM CHLORIDE CRYSTAL ELEMENTS

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Summary

A new type of hygrometer, which has been termed the electrolytic condensation hygrometer, was described in the first of the present two papers. Its capabilities and limitations depend mainly on the characteristics of the conducting liquid layer formed on the surface of the crystal element used; these characteristics depend in turn on those of the surface of the crystal. A detailed experimental investigation has been made of the relevant properties of potassium chloride crystal elements. An explanation of these properties in terms of the structure of the crystal surface is given. This may be used as a basis for predicting the behaviour to be expected of the hygrometer for a wide range of conditions. It has been concluded that at ordinary temperatures the method is capable of an absolute accuracy in the equilibrium temperature (or corresponding dew-point) of $0.01\text{ }^{\circ}\text{C}$, is capable of detecting changes in that temperature of $0.002\text{ }^{\circ}\text{C}$, and is capable of a time-constant of as little as a second.

In addition to providing direct information on the behaviour of the hygrometer the experiments have revealed fundamental effects of some interest. The most significant of these demonstrate the existence of free energy barriers to crystal growth and crystal dissolution. Evidence has been obtained that the vapour pressure of a layer of saturated solution only 80 \AA thick does not differ from that of the bulk liquid by more than 0.15 per cent.

I. INTRODUCTION

This is the second of two papers dealing with the physics of a new method of hygrometry. The previous paper (Wylie 1957) was concerned with the essentials of the method, with its relationship to conventional methods, and with its general theoretical aspects. A general outline of the behaviour of the crystal element was given, based on experience with several crystal substances. At ordinary temperatures and to an accuracy of $0.1\text{ }^{\circ}\text{C}$ in the equilibrium temperature (or corresponding dew-point), the behaviour of the crystal element is found to follow the theoretical ideal within a wide resistance range, but at higher accuracies secondary effects may be observed. As these effects, which arise entirely from the crystal element, largely determine the ultimate capabilities and limitations of the method, it is desirable to study them in some detail.

The emphasis in the present paper is, therefore, on the equilibrium between the crystal, the conducting liquid layer, and the surrounding gas. To understand the detailed behaviour of the crystal element a study must be made of the nature and properties of the liquid layer and in particular the extent to which that layer

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may be regarded as a quiescent plane sheet of the ordinary saturated solution. The present paper gives an account of such a study.

In the experiments to be described the number of variables was kept to a minimum by using a single crystal substance, namely potassium chloride, and by working at practically a single temperature. From the results it has been possible to deduce the relevant properties of the liquid layer and hence those of the crystal element.

Some of the results show in a more or less direct way the behaviour to be expected of hygrometers employing potassium chloride crystal elements, but, what is more important, when interpreted theoretically in terms of the detailed structure of the crystal surface they lead to a general understanding of the phenomena associated with the liquid layer. On the basis of this the characteristics of the hygrometer may be predicted, at least in a general way, for a wide range of conditions of use. In particular, the characteristics of crystal elements of different substances may be expected to differ in degree rather than in kind; experience indicates that this is so and that the observed differences, which are generally not large, correlate as expected with differences in the properties of the respective saturated solutions.

The use of an electrical method to detect the liquid layer and of an isothermal enclosure to house the crystal element has made the attainment of a very high sensitivity a relatively simple matter. The temperature sensitivity achieved (about 0.001°C) has revealed effects which are of interest in themselves and some of which have not previously been observed. For example, what is believed to be the first experimental evidence that a crystal surface can present free energy barriers to dissolution has been obtained.

From the experimental results it can be concluded that at ordinary temperatures the method is capable of an absolute accuracy in the equilibrium temperature (or in the corresponding dew-point) of 0.01°C , can detect changes in that temperature of 0.002°C or smaller, and can at the same time respond to humidity changes in as little as 1 sec. The observed sensitivity is in satisfactory agreement with the theoretical sensitivity derived in the previous paper.

II. APPARATUS

The experiments were performed by operating crystal elements in a hygrometer constructed specifically for investigational purposes and consisting of thermal and electronic units which will be described elsewhere. The thermal unit was of the form illustrated in Figure 2 (*a*) of the previous paper. The crystal enclosure was of silver and was cooled by the expansion of carbon dioxide. The electronic unit provided wholly automatic operation.

The electronic unit contained, in effect, an A.C. resistance bridge, one arm of which was provided by the crystal element, and a second bridge in which one arm was a resistance thermometer wound on the metal enclosure. In ordinary operation the out-of-balance voltages of both bridges played a role in governing the heat supplied to the thermal unit to maintain the equilibrium temperature. However, the arrangement had the property that, when a fixed resistor was substituted for the crystal element, the temperature of the crystal enclosure

could be maintained at any desired value by setting one arm of the resistance thermometer bridge appropriately. The power exchanged between the heater and the cooling system was only 0.16 W.

The temperature of the enclosure was indicated by a meter associated with the circuit of the second bridge. The meter covered a range of 1 °C, which could be adjusted to any desired temperature. Its response was closely linear. In addition, the temperature could be recorded continuously on a General Electric Company photoelectric recorder (Type 32C120). Its sensitivity was such that changes of 0.002 °C could be satisfactorily recorded. The bridge assembly was calibrated at 0 °C and at 20 °C, special attention being given to the former calibration point since most work was done at an equilibrium temperature of approximately 1.7 °C. The calibration at 0 °C was effected by controlling the

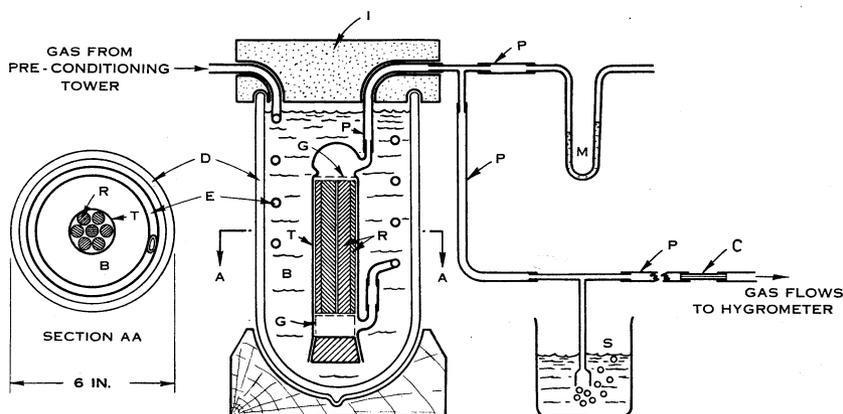


Fig. 1.—Conditioning system which equilibrates gas with ice at 0 °C. The tower *T*, which contains rods of ice *R*, is surrounded by the ice-water mixture *B*. *G*, copper gauze; *S*, pressure regulator; *C*, capillary constriction to stabilize rate of flow; *D*, Dewar vessel; *E*, heat exchanger; *I*, insulation; *P*, flexible polythene tubing; *M*, manometer.

temperature of the crystal enclosure at each of a succession of temperatures differing by only a few thousandths of a centigrade degree and observing the setting of the resistance thermometer bridge at which a group of small ice crystals placed in the crystal cavity melted.

An important part of the apparatus was the system in which gas was conditioned for use in tests on the hygrometer. It was found that it was easy to obtain a vapour pressure constant to 1 per cent. by passing the gas (oxygen from a commercial cylinder) through crushed ice which was not waterlogged, but that great care was necessary to improve this accuracy by a factor of 10, as was required.

Complete success in this respect was achieved by pre-conditioning the gas in a tower containing crushed ice and then passing it through the apparatus shown diagrammatically in Figure 1, a tower *T* containing seven rods of ice *R*. These rods, which were about 6 in. long, were prepared by compacting crushed distilled-water ice in a tube and were assembled as shown in the figure. The

tower was fully immersed in an ice-water mixture *B* and could be kept in good condition for a week or more without renewal of the rods. Precautions were taken to eliminate initial condensation inside the outlet tube of the second tower. The gas from the pre-conditioning tower, which was also immersed in an ice-water mush, was always found to be more moist than would be expected. A simple pressure regulator *S* permitted the flow of gas in the conditioning system to be varied independently of that in the hygrometer. The partial pressure of the water vapour in the gas issuing from this device was found to be constant and independent of the rate of flow of gas in the system, at least up to a flow rate of 25 cm³/sec. Although the pressure drop required to produce the desired flow of about 2.5 cm³/sec through the hygrometer (corresponding to a mean gas velocity in the crystal cavity of 9 cm/sec) was only about 2 mm of water gauge, the overall drop was increased to 10.5 mm of water gauge at this flow rate by inserting the capillary tube *C*. The pressure drop was indicated by the manometer *M*, which contained dibutyl phthalate, and served as a measure of the flow. A small correction was applied for the difference in total pressure between the inside of the ice-rod tower and the crystal cavity of the hygrometer. Since the pressure in the crystal cavity differed negligibly from atmospheric pressure, this pressure difference was simply that indicated by the manometer; a reading of 10.5 mm of water gauge corresponded to a reduction of 0.10 per cent. in vapour pressure.

Interconnecting tubing of polythene was used where some flexibility was desirable and is shown by the letter *P* in Figure 1. Rigid connections were of glass or metal. Experience has shown that rubber tubing is quite unsuitable for the conveyance of gas which has been accurately humidity conditioned.

III. THE CRYSTAL ELEMENT

Potassium chloride was selected for the crystal substance because it is readily available in a pure state, can easily be cleaved into blocks of accurately rectangular shape bounded by habit faces, and is very stable chemically. Moreover, this substance is very suitable for routine hygrometric measurements; probably its only disadvantage is that it cannot be used when the dew-point temperature is below about -11.5°C .

The crystal elements used, which were about 2.5 mm square in section and 3 mm long in the direction of electrical conduction, were prepared by the method outlined in the previous paper. The crystal faces approximated (100) and similar planes. The elements were end-coated with gold by vacuum evaporation, the gold coating extending onto three conduction faces. It is believed that, for the range of electrical conductance of significance here, very little contribution to the conductance of the element is made by the face onto which the gold does not extend. To ensure the greatest cleanliness, each completed crystal element was washed, before use, in pure ethyl alcohol, in which potassium chloride is practically insoluble, although the properties of elements prepared with reasonable care were found to be unchanged by this procedure.

Potassium chloride surfaces which have been freshly prepared by cleavage or freshly washed in pure methyl or ethyl alcohol have been found to exhibit

some remarkable properties with respect to water. In Appendix I, where these properties are described, it is explained that the peculiarities disappear after a period of standing and that thereafter the surface exhibits unchanging properties which are favourable for the application of the crystal in hygrometry. All the experiments were performed with crystal elements which had been "seasoned" by standing and had been then subjected to operation in the automatic hygrometer with repeated changes in the resistance of operation.

IV. THE EXPERIMENTS

The properties of the liquid layer which must be known in order to understand the behaviour of the crystal element are those which determine its real or apparent vapour pressure. The vapour pressure may differ from that of the bulk saturated solution on account of curvature of the free surface of the layer and, if the layer is thin enough, on account of its small thickness. Also, an apparent change in vapour pressure may be observed if a continuous change occurs in the layer, as may happen, for example, when the liquid flows under the influence of surface tension forces. It is, therefore, desirable to obtain information concerning the structure of the layer.

It is probably impracticable to measure the vapour pressure of the layer by conventional means after establishing the desired resistance and temperature. However, the dependence of the vapour pressure on resistance, for example, can be determined indirectly by operating the crystal element in the hygrometer using gas of accurately constant water vapour pressure and observing the temperature at which the resistance becomes constant for each of a succession of resistance values. Such an experiment is greatly facilitated by automatic operation of the hygrometer, the temperature being brought automatically to the value at which the resistance, set by the observer, remains constant. By this means changes of temperature rather than changes of vapour pressure are observed, the relation between them being easily derived from data given in Table 1 of the previous paper.

Typical results for an experiment of this type, in which the temperature was allowed to come to a steady value at each of a succession of different resistance values, are given below. In the interpretation which will be given, the transient effects observed are attributed to the flow of the liquid layer to or from steps which exist on the crystal surface. This implies that they represent apparent rather than real changes in vapour pressure. Such differences as exist between the steady temperatures reached at different resistance values will be attributed to a real vapour pressure lowering due to a general small-scale concavity of the liquid surface which increases with the resistance.

Other experiments test the linearity of the increase in conductance of the crystal element with the time integral of the deviation of the temperature from the equilibrium value. In addition to showing that the integrating property is followed with remarkable precision except at high resistances and providing experimental values for the sensitivity, the results reveal effects due to the existence of free energy barriers to crystal growth and crystal dissolution and

exhibit features which can be related quantitatively to the same surface steps as give rise to the transients referred to above.

The effects of the presence of a soluble contaminant on the crystal surface and also of an oily contaminant are examined. The results for the former provide valuable information concerning the true thickness of the liquid layer. The several experiments will be described in turn and will then be considered theoretically. Except where otherwise specified the crystal elements were end-coated with gold, the equilibrium temperature was approximately 1.7°C , and the mean velocity of the gas passing over the crystal element was approximately 9 cm/sec (corresponding to a flow of $2.4\text{ cm}^3/\text{sec}$).

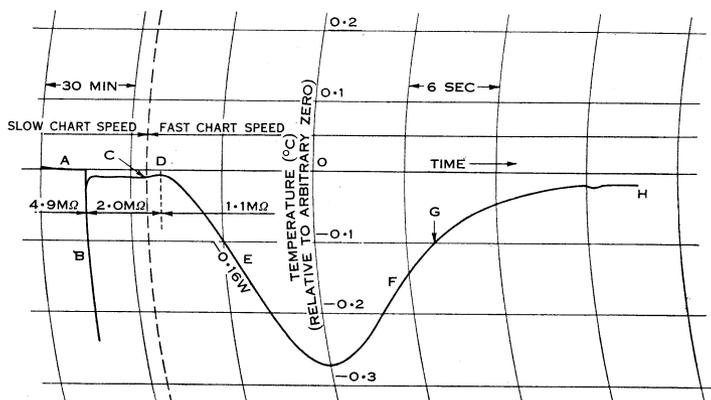


Fig. 2.—Recorded temperature transients representing sudden large reductions of the resistance set on the control unit.

(a) *The Approach to Equilibrium*

When a hygrometer of the present type is operated automatically the resistance of the crystal element remains practically constant while the temperature varies in such a manner as to maintain that resistance. Variations in temperature occur, of course, if changes occur in the humidity of the gas passing over the crystal element, but even when the humidity is constant they may occur as a result of more or less spontaneous changes in the structure of the surface layer of saturated solution. Changes of the latter type occur transiently following the resetting of the resistance of operation to a markedly different value and a study has been made of the associated temperature variations.

When the resistance selector was reset to an appreciably different value the first temperature changes which occurred were those necessary to build up or reduce the liquid layer to the new thickness. Only the subsequent changes, which occurred after the new resistance value had been established, represent the properties of the crystal element which were being investigated. In order to show the form of the whole temperature transient associated with such a resistance transition and the relationship of the subsequent temperature drift to the initial part of the transient, an example recorded at a fast chart speed is given in Figure 2. The point *D* marks the resetting of the selector from 2.0 to $1.1\text{ M}\Omega$. After one

or two seconds the temperature is falling rapidly and at *E* the rate of fall is very closely that to be expected on the basis of the power level and the calculated thermal capacity of the crystal enclosure. This constant rate of fall gives way to a rise as the heater power swings from zero to a value of about 0.3 W and then returns to its initial value of 0.16 W. This initial phase of the transient, which is characterized by considerable changes in the actual resistance of the crystal element, is governed by the dynamics of the whole system and the level of heating (or cooling) power; it pertains more to the thermal properties of the hygrometer unit than to the characteristics of the crystal element and will be discussed in a subsequent paper in conjunction with a description of the electronic control unit. The initial phase is effectively complete at the point *G* where the resistance of the crystal element has attained a value of 1.1 M Ω and the thickness of the con-

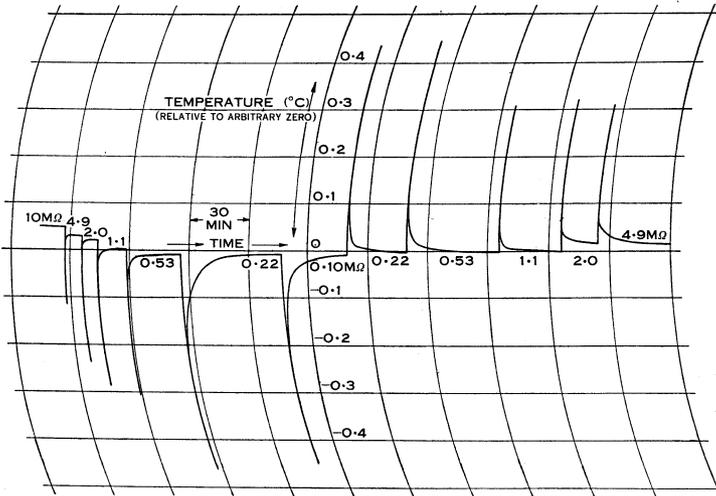


Fig. 3.—Recorded temperature changes for a succession of changes in the resistance of the crystal element.

ducting layer has been approximately doubled. The subsequent change, extending from *G* to *H* and perhaps far beyond, is characterized by a constant resistance of the crystal element and a comparatively slow approach of the temperature to a steady value and is the result of secondary effects occurring on the crystal surface. The curve *ABC*, given in Figure 2, represents a preceding resistance step and shows a complete transient when recorded at the slow chart speed used in all following experiments.

The way in which the transient and the steady temperature attained depend on the resistance and the direction in which that resistance is approached is shown in Figure 3 for a succession of resistance steps, each involving an approximately twofold change in resistance. Curves such as these reproduce reasonably well in successive experiments on one individual crystal element but differ significantly, although not markedly, in experiments on different, nominally identical elements.

The general features of such a set of resistance-transition curves have been found to be as follows. A change in the character of the curves for downward resistance steps occurs at about the 1-0.5 M Ω step. The transition curves for higher resistances show an initial and sometimes very rapid recovery to higher temperatures followed by either a very slow downward drift or else an apparently steady temperature which decreases with decreasing resistance. The curves corresponding to steps below the 1-0.5 M Ω step show a considerably slower recovery which is always to higher temperatures and which usually becomes yet slower as one goes to lower resistances. The curves for upward resistance steps are somewhat different in character to those for downward steps; the rate of approach to equilibrium is, in general, less.

The true thermodynamic equilibrium temperature, T_e , can be deduced with high precision from such a set of transition curves. In Figure 3 the temperature T_e lies at approximately 0.01 °C below the arbitrary zero. It is usually found that the curve for the 1-0.5 M Ω transition approaches this value closely and rapidly. When, after reaching a resistance of 0.1 M Ω , the first upward resistance step is made, to a value of 0.2 M Ω , it is usually found, also, that a rapid and close approach is made to T_e . In the following successive upward steps there is a tendency for recovery towards T_e to occur over a longer period than in the corresponding steps of the downward progression. The results of numerous experiments suggest that, at least in respect of resistances of 0.1 and 0.2 M Ω , the approach to the equilibrium temperature continues while a measurable temperature difference remains. The temperature T_e can be determined with an accuracy of ± 0.01 °C or better from any individual transition curve for a resistance of from 0.1 to 1.0 M Ω .

With a few crystal elements the observed steady temperatures were found to be the same within 0.01 °C up to rather higher resistances (e.g. 10 M Ω). These crystals possessed visually perfect surfaces, but others, which also possessed such surfaces, gave a more typical performance approximating that of Figure 3.

Crystals end-coated with graphite instead of gold are found to possess characteristics similar to those described above, but to vary more in their behaviour from element to element. The increase in recorded steady temperatures obtained on returning to high resistances is sometimes several hundredths of a degree greater than for crystals with gold electrodes. It is found that this effect can usually be eliminated by carefully washing the crystal elements in ethyl alcohol.

It should be noted that the time associated with the quite large resistance transitions involved in the present type of experiment bears little relation to the response time of the hygrometer for changes in humidity; this will be established below.

(b) The Dependence of Apparent Equilibrium Temperature on Resistance

The way in which the apparently steady temperatures attained in experiments such as those just described depend on the resistance is shown in Figure 4, where graph (a) represents the data of Figure 3 and graph (b) represents similar data obtained with another crystal element. The data plotted in (c) were obtained

with the crystal element of (b) after it had been contaminated by painting with a 1 per cent. solution of sodium thiosulphate (which, as will be shown below, greatly changed its properties) and then reconditioned by washing it in ethyl alcohol. Because in some cases the approach to a steady temperature was very protracted, each of the temperatures plotted in the graphs of Figure 4 is the value relating to a time 30 min after the change in resistance setting was made.

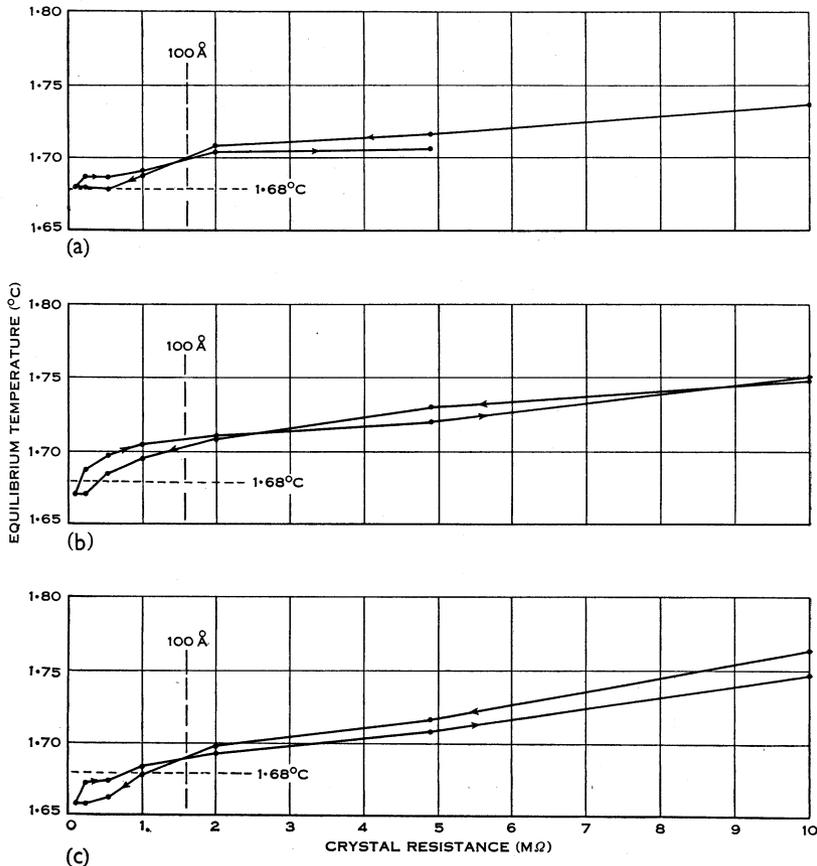


Fig. 4.—Plots of the apparently steady temperatures reached in a succession of resistance changes. (a) and (b) Different crystal elements. (c) Element of (b) after contamination and reconditioning.

Had it been practicable to await the attainment of really steady temperatures the “hysteresis loops” apparent at low resistances in the figure would have been much smaller if not completely absent.

In principle, accurate values of T_e can be deduced by extrapolating the graphs of Figure 4 to zero resistance, but comparison of Figures 3 and 4 shows that the approach curves of the former figure give a more accurate indication of the true value of T_e than can be obtained by such an extrapolation. However, if the crystal is significantly contaminated with soluble matter the extrapolation

procedure can be used to good advantage, as will be shown below. The curves given are believed to represent the behaviour of crystal elements which are free of soluble contaminants. A comparison of curves (b) and (c) shows how thoroughly some forms of contamination can be removed by washing the elements in ethyl alcohol.

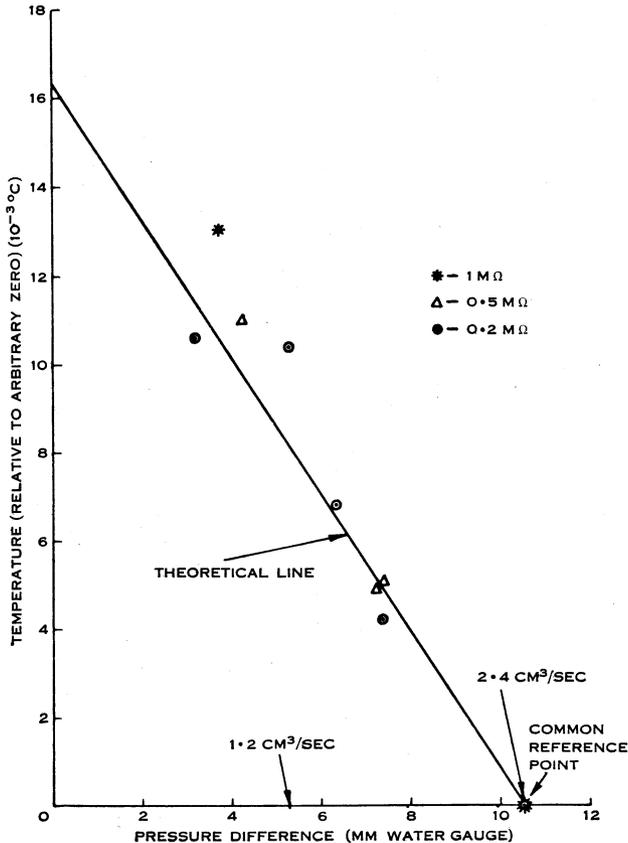


Fig. 5.—Equilibrium temperature as a function of gas flow rate. The full line shows the expected effect due to the pressure. The agreement between the plotted points and the line shows that no significant effect results from changing the rate of flow of gas over the crystal element.

(c) The Effect of the Rate of Flow of the Gas

Experiments were performed to determine whether the observed equilibrium temperature depends on the rate of flow of gas in the hygrometer. The results are plotted in Figure 5. To obtain these results the relative accuracy of the apparatus was taxed to the limit, the recorder deflection being estimated to one-twentieth of a division (0.001 °C) and corrections being applied for small drifts which occurred during the measurements.

The straight line drawn in the figure is the locus expected theoretically on the basis of the expansion of the gas from the excess pressure indicated by the

manometer shown in Figure 1. The agreement is good and indicates the absence of any significant intrinsic effect of the rate of flow on the observed equilibrium temperature.

(d) *The Observed Sensitivity*

To determine experimentally the relationship between the rate of change of the crystal conductance and the deviation of the temperature from the equilibrium value the apparatus was modified so that the temperature of the crystal enclosure could be controlled closely without regard to the crystal conductance. The apparatus was so arranged that the temperature could first be brought automatically to the equilibrium value in the usual way and then, by throwing a switch, could suddenly be changed to a steady value differing

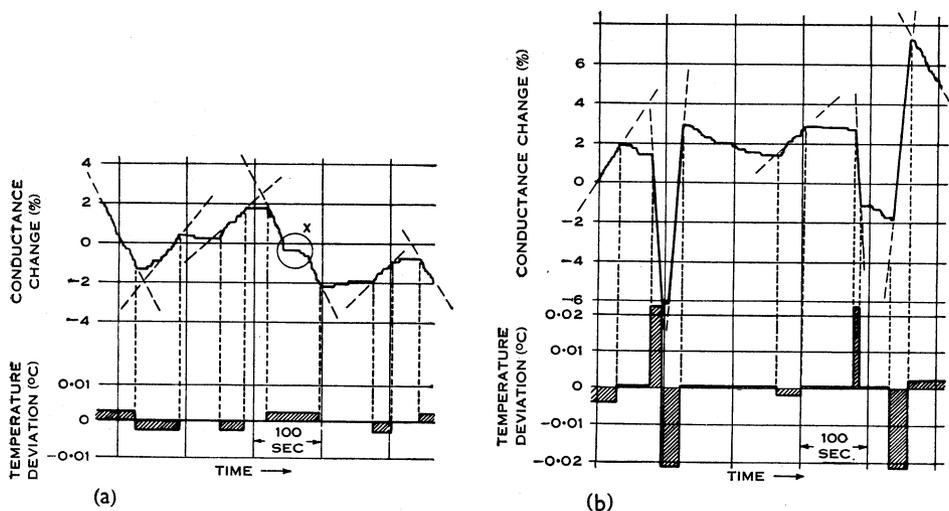


Fig. 6.—Recorded conductance-drift curves for small deviations of the temperature from the equilibrium value. Nominal resistance $1\text{ M}\Omega$. (a) shows the repeatability and reversibility of the drift rate for very small temperature deviations. (b) shows that, at $1\text{ M}\Omega$, slow drifts are little affected by rapid drifts which immediately precede them.

from the equilibrium value by any desired amount. Simultaneously the conductance of the crystal was recorded on a high-speed potentiometric recorder. The displacement of the temperature could be effected in about 1 sec.

Figure 6 shows, as a function of time, the temperature deviations imposed on two crystal elements and the resulting conductance changes; the nominal resistance in each case was $1\text{ M}\Omega$. The crystals used were end-coated with gold. The figure shows that a departure from the equilibrium temperature of as little as 0.002°C produces a definite and approximately uniform drift in conductance. The irregularly marked X is probably due to an extraneous disturbance, although such discontinuous changes have sometimes been found to arise from the crystal element, especially with crystals held between separate electrodes as described earlier (Wylie 1955).

When the equilibrium temperature is re-established following a rapid drift to higher resistances at a nominal resistance of $2\text{ M}\Omega$, a counter-drift to lower

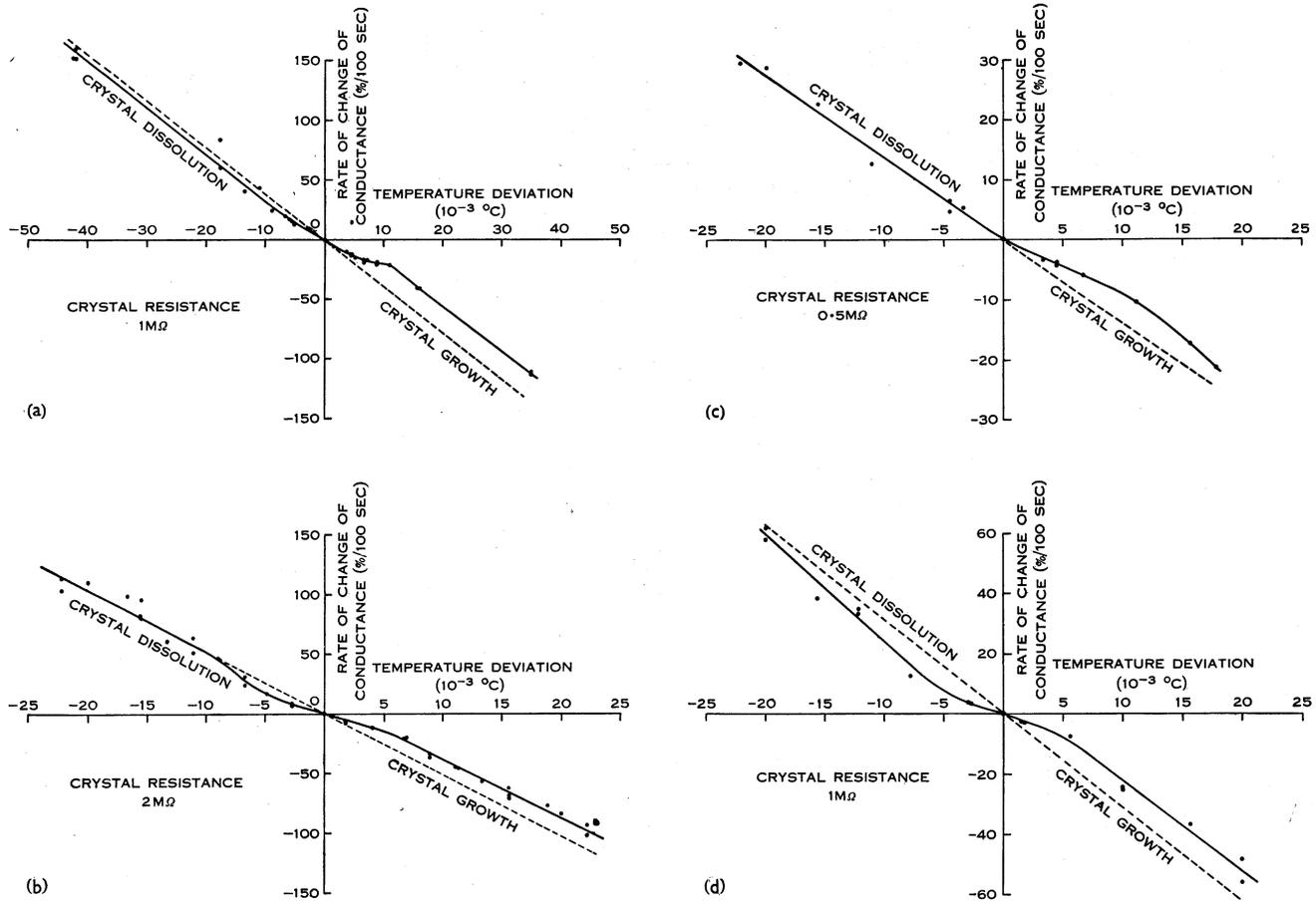


Fig. 7.—Plots of conductance drift rate against temperature deviation. (a) and (b) relate to one crystal element and (c) and (d) to another.

resistances, which dies away after some seconds, is often observed. The effect is hardly perceptible for changes of the opposite sense. Rapid drifts to higher resistances usually diminish in rate as the resistance change progresses although in an initial period of the order of half a minute the rate of drift is constant. At progressively higher resistances above 2 M Ω , the recovery effect and especially the falling away in drift rate increase in prominence and the effects are soon observed for changes of the opposite sense. At these resistances the sensitivity increases more and more slowly with resistance as the resistance is increased. At a resistance of 10 M Ω no part of a recorded drift curve is a straight line.

By recording the drift in conductance for each of a series of temperature deviations data were obtained from which curves such as those of Figure 7 could be plotted. The figure relates to two different crystals end-coated with gold. The broken reference line associated with each curve is a straight line through the origin possessing the general slope of the curve. Curves (a) and (b), unlike (c) and (d) which relate to the second crystal element, are derived from drift curves which alternate with constant resistance traces obtained at the equilibrium temperature. Thus any recovery effect which followed the drift corresponding to a particular point plotted in (c) or (d) has been superimposed on the drift curve represented by another point plotted on the same curve. For this reason it is desirable to state the order in which the data were obtained, which was, in terms of the plotted points, from the origin outwards and alternating in sign. Plots (c) and (d), therefore, indicate in a particularly direct way the behaviour to be expected of the crystal element during automatic operation of the hygrometer, when small variations in temperature occur continuously.

Figures 6 and 7 are of considerable significance for the performance of the hygrometer and especially its speed of response. The four curves of Figure 7 reveal that the rate of drift is correlated with the temperature with an accuracy of about 0.001 °C. The continuity of the curves at the origin and the fact, apparent in all of them, that the sensitivity does not diminish markedly as the temperature deviation approaches zero, are important features. At the same time, the curves provide examples of a resistance to crystal growth, probably the first examples of a resistance to crystal dissolution, an example of an abrupt change in the growth regime, and examples in which the growth rate does not appear to return to the expected law at high rates. They also show that a measurable dissolution resistance does not necessarily occur. These aspects will be considered in detail below.

(e) *The Effect of a Soluble Contaminant*

If a soluble contaminant is present on the crystal surface it affects the composition and hence the equilibrium vapour pressure of the conducting layer. In the simplest view the amount of contaminant in the layer remains constant as the layer thickness is varied and the concentration of the contaminant, assumed to be wholly dissolved, varies inversely as the thickness. If, while the layer remains in equilibrium with the crystal, the vapour pressure is a linear function of the concentration of contaminant, then, for small degrees of contamination, the observed equilibrium temperature is a linear function of the electrical

resistance. In any case, as the resistance approaches zero the resistance-temperature curve should extrapolate to the thermodynamic equilibrium temperature for a clean crystal.

To test the validity of the extrapolation procedure potassium chloride crystals were contaminated deliberately by "painting" them lightly with a 1 per cent. solution of sodium thiosulphate. A typical example of the resulting resistance-temperature curve together with the curve for the same crystal after washing in pure ethyl alcohol is shown in Figure 8. The branch of the curve for downward resistance steps, which is quite distinct from that for upward

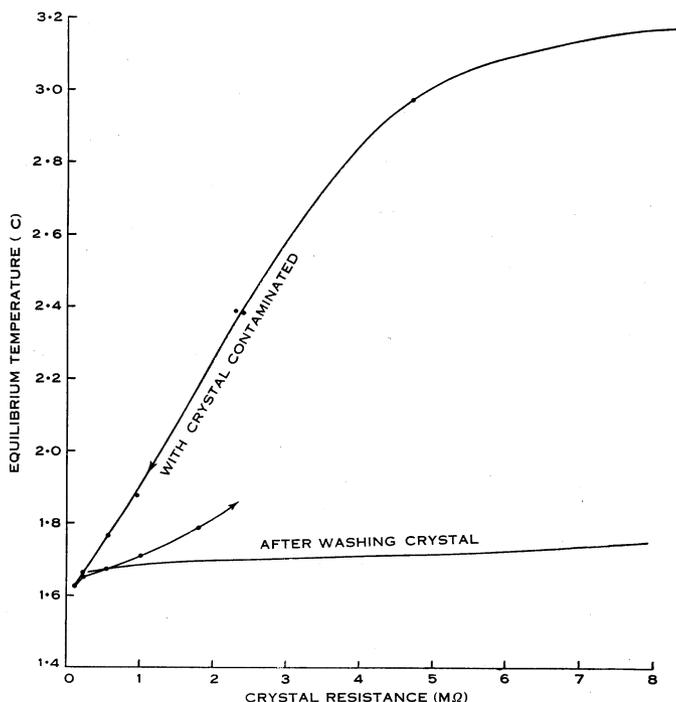


Fig. 8.—Plots of equilibrium temperature against resistance for a crystal element deliberately contaminated with sodium thiosulphate and for the same element after washing in ethyl alcohol.

steps, is approximately linear except above about 4 MΩ. The two branches and the curve for the washed crystal have, very nearly, a common point of intersection. The fact that this point is not quite on the temperature axis is probably due to the neglect of long-term recovery effects, as in Figure 4, and the lapse of 3 days between the experiment with the contaminated crystal and that performed after washing.

The results point to the fact, confirmed in other experiments, that, in order to obtain a continuous plot of temperature against resistance with a contaminated crystal, the resistance steps must be made in a regular sequence. The temperature derived by extrapolating data obtained with a heavily contaminated crystal is

not as accurate as may be derived from results obtained with a clean crystal but is much more accurate than the measured equilibrium temperature at, say, 2 M Ω . The degree of contamination represented by Figure 8 is not likely to be acquired accidentally. It is found that crystal elements prepared with ordinary care, which give a performance such as that represented by the curve for the washed crystal, show no evidence of change in behaviour after the hygrometer has been operated for some days on room air.

(f) *The Effect of Oleic Acid*

To determine the effect of a contaminant which is able to spread on the surface of the saturated solution, experiments were performed in which crystal elements were contaminated with oleic acid. Even at temperatures well below its melting point (about 14 °C) oleic acid spreads strongly on a saturated solution of potassium chloride. Visible globules of the oil, which does not wet the apparently dry crystal surface, were applied to the (four) bare faces of crystals end-coated with gold. To ensure the formation of a monolayer of oil over the whole of each such face, the faces were then breathed on in turn to produce a visible liquid layer.

The approach curves for resistance transitions and the resulting resistance-temperature plots were found to be the same as for crystals to which no oil had been applied. Nor was there any appreciable difference in sensitivity, that is, in the rate of change of layer thickness, as compared with a nominally clean crystal.

V. CONSIDERATION OF THE RESULTS

(a) *Quantitative Comparisons*

Before considering the various effects which the experiments have revealed, the observed equilibrium temperature will be compared with a value calculated from the known relative vapour pressure of saturated potassium chloride solution and the theoretical sensitivity compared with that observed.

The first comparison is hampered by the accumulation of uncertainties in the factors involved. The best estimate which can be made at present of the relative vapour pressure of the saturated solution at approximately 1.7 °C is 0.885 ± 0.002 . Allowing for the expansion of the gas from the ice tower to the hygrometer, the dew-point is -0.014 °C. The equilibrium temperature can be computed from these values once it is known how the vapour pressure of water varies with temperature. Using data tabulated in the Smithsonian Meteorological Tables (Smithsonian Institution 1951), based on the work of Goff and Gratch (1946), the resulting equilibrium temperature is 1.68 ± 0.03 °C. For the experimental value the mean of three values obtained from the data represented by Figure 4 may be used. The result is 1.67 ± 0.02 °C in which the uncertainty arises mainly from some instability of the temperature indication.

The slopes of the curves of Figure 7, as defined by the broken lines, provide experimental values for the sensitivity, which may be expressed as the percentage rate of change of conductance per 0.1 °C temperature deviation. These values are given in Table 1, where they may be compared with the theoretical values

derived from the appropriate value of J given in Table 1 of the previous paper. When account is taken of the many factors involved in deducing the theoretical values and the uncertainties which some of those factors introduce, the agreement must be considered satisfactory.

TABLE 1
PERCENTAGE RATE OF CHANGE OF CONDUCTANCE PER SECOND, PER 0.1 °C
DEVIATION

Resistance (MΩ)	Layer Thickness (Å)	Observed Sensitivity	Theoretical Sensitivity
0.47	320	1.4	2.2
1.1	140	3.1	5.2
1.1	140	3.9	5.2
2.2	70	5.2	10.4

(b) *The Explanation of the Results*

Any explanation of the behaviour of the crystal element must involve the detailed geometry of the crystal surface. The cleft surface occasionally possesses steps visible to the naked eye, but even when apparently perfect it must be considered rough on a molecular scale, deviating from a (100)-like plane at least as dictated by the dislocation structure of the parent crystal. The structure of cleft surfaces of sodium chloride has been investigated by Amelinckx (1951), who observed steps ranging in height from some hundreds to some thousands of ångström units. These were not necessarily parallel to an axis of the crystal and ranged in spacing from 10^{-3} to 10^{-2} cm. He also observed evidence of a fine structure involving changes of level of up to 200 Å.

Preliminary operation of the crystals in the automatic hygrometer at various resistances must have modified their surface structure. Also, the prolonged operation at a single resistance which preceded some experiments (notably those of Figs. 5, 6, and 7) would have resulted in any small features which protruded from the (100)-like surface dissolving even in the just-saturated solution. This fact, although strictly thermodynamic in origin, may be regarded as following from the theory of crystal growth, which will be involved in some of the discussion below.

Crystals usually grow from solution by the mechanism first proposed by Frank (1949). In the Frank mechanism crystal substance deposits at steps which terminate on dislocation axes and so are inevitably present. Such a step, since it is in general curved and possesses a line free energy, is associated with an elevation or lowering of equilibrium concentration in the solution. It is, therefore, analogous to a very small crystal, the equilibrium vapour pressure (or in a solution, concentration) of which is elevated on account of its surface free energy. It was necessary to propose this mechanism because, as is deducible from the work of Becker and Döring (1935), nucleation of a new plate of molecules on a flawless crystal surface as substrate cannot possibly occur at supersaturations

of only a few per cent., while the possibility of the mechanism depends, in the first instance, on the fact, deducible from the same work (their equation (20)), that nucleation of a new row of molecules at a straight step is very easy. The basic theory, along with some related matters, has been treated in detail by Burton, Cabrera, and Frank (1951). Although the theory is valid strictly only for crystals the elementary units of which are bound by short-range forces, it will be assumed here that the essential conclusions are valid also for ionic crystals, as is generally believed.

Repeated dissolution and regrowth, in the present circumstances, would have tended to level the original fine structure by transferring material from the crests to the troughs where it could deposit, beginning at the bottom of each step. Surface features of even many thousands of ångström units extent in the plane of the surface would be expected to dissolve in the just-saturated solution in a time much shorter than the periods of stabilization which preceded the experiments of Figures 5, 6, and 7. Elimination of the fine structure in these ways would lead to a surface of minimum roughness, the form of which would depend on the strength and number of the dislocations present.

In experiments like that of Figure 3 the rapid growth and dissolution associated with rapid large resistance changes would be expected to produce respectively growth spirals and pits which, when the resistance became constant, would tend slowly to disappear. The tendency of the features to "run back" after a rapid movement must have made some contribution to the slow recovery effects exemplified in Figure 3. However, since on changing from 0.53 to 0.22 M Ω an effect of magnitude 0.2 °C, which would correspond to a deviation from saturation of about 10 per cent., decays with a time-constant of about 10 min, it is clear that this contribution provides only a very small part of the effect. Of even a large growth or dissolution feature, only a central part of about 100 Å radius could provide such a large effect and this part would very quickly disappear. The slow recovery effect of Figure 3 is due to the accretion of the liquid, in the form of fillets, at the bases of high steps.

If the surface is regarded as possessing a coarse step structure, as observed by Amelineckx (1951), and the fine structure considered above, the phenomena of Figure 3 may be explained in a general way as follows. The whole resistance range may be divided into three parts, namely, below about 0.5 M Ω , from about 0.5 to 2 M Ω , and above about 2 M Ω . Not much can be said concerning the highest range, in which the resistance yields unreliable information concerning the amount of liquid present on the surface. The significance of the value 2 M Ω is shown by the fact that, generally, above this value a contamination plot (Fig. 8) becomes non-linear, a rate-of-drift experiment becomes markedly affected by inconstancy of the drift rate and by counter-drift effects, and the observed sensitivity (as given for lower resistances in Table 1) deviates more and more markedly from the theoretical value.

It is considered that, in this range, the liquid does not cover the whole surface but is in the form of fillets which are largely interconnected by intersection, and between which there exists only the inevitable adsorption layer consisting of a thin sheet of modified solution. The experiments provide no basis for

determining above what resistance the conduction in the adsorption layer preponderates over that in the system of fillets. The total curvature of the free surface of the liquid fillets is, for this range, constant over the crystal surface, corresponding to a uniform vapour pressure lowering given approximately by the following equation, which is little different from the Kelvin-Poynting equation :

$$kT \ln \{(p + \Delta p)/p\} = \sigma \gamma v, \dots\dots\dots (1)$$

where p is the vapour pressure over a plane surface of the saturated solution, Δp is the vapour pressure difference, γ is the surface tension, v is the partial molecular volume of water in the solution, σ is the total curvature, and k is Boltzmann's constant. Equation (1) neglects a smaller effect due to the simultaneous application of the excess internal pressure of the liquid to both the liquid itself and the underlying crystal. The vapour pressure lowering corresponds to the slightly elevated steady temperatures observed in the high resistance range (Fig. 3). The equilibrium between the solution, the adjacent gas, and the adsorption layer is a true one ; steady conditions are reached quickly, the liquid then being quiescent.

The resistance range of roughly 2 to 0.5 M Ω is characterized generally by a linear contamination plot, which extrapolates to the true equilibrium temperature at zero resistance (Fig. 8), by a well-defined linear relationship between rate-of-drift and temperature deviation (apart from small effects) (Figs. 6 and 7), and by an observed sensitivity in good agreement with the theoretical value ; such lack of agreement as exists apparently does not depend noticeably on the layer thickness (Table 1). The steady temperatures reached are still slightly elevated. An obvious deduction is that in this range the crystal surface is completely covered by the liquid. The elevation of the observed steady temperatures can be explained by assuming the surface fine structure to be higher than the liquid layer, which, in reaching up to the crests, must present a surface consisting of numerous concave areas. Since, as Figure 3 shows, the temperature elevation has disappeared when the resistance has been reduced to 0.5 M Ω , the height of the fine structure would be about 200 Å, a value which must relate to the minimum structure, maintained by dislocations. The temperature elevation of 0.02 °C at 2 M Ω (Fig. 3) would, in accordance with equation (1), require a mean separation of the crests of the order of 4000 Å. Such a structure would represent a preponderance of dislocations of one sign (dislocations being weighted in proportion to their strength) of about 30 elementary distances in regions averaging 1.6×10^{-9} cm² in area. The necessary concentration of dislocations seems high, but there appears to be no alternative postulate which can provide a satisfactory alternative to this fine structure, on the basis of which all the observed phenomena are explainable.

The average layer thickness derived from the resistance is subject to some uncertainty on account of the existence of high steps. However, a geometrical factor of less than 2 would be sufficient to produce virtually complete agreement between the observed and calculated sensitivities given in Table 1. Also, Figure 8 shows that the geometrical factor must be constant for resistances lower than about 2 M Ω ; it can hardly differ much from unity. It may be

thought that Table 1 provides a comparison of theoretical and observed percentage rates of change which are derived quite independently. However, the theoretical percentage rate involves a layer thickness derived from the electrical resistance. Actually, the table represents a comparison of absolute rates of growth (or dissolution) of the surface layer. The only experiment which gives accurate information on percentage changes in the amount of liquid on the surface is that of Figure 8, which is of some importance on this account.

In the range below about $0.5 \text{ M}\Omega$, the liquid completely submerges the fine structure and hence presents an almost plane surface. Its thickness and mobility are such, however, that fillets form at an appreciable rate at the coarse steps. Until these fillets grow to such a size as to present only a very small surface curvature, the liquid which they absorb must continually be replaced, through the maintenance of a temperature below the true equilibrium value. This explains the slow approach phenomena of Figure 3. The reverse process explains the slow approaches on returning to high resistances. Since the resistance to flow in the layer varies as the cube of layer thickness, a large fillet formed at a low resistance tends to be "frozen-in" if two or more upwards resistance steps are subsequently made in a short time. For the resistance sequence of Figures 3 and 8 the fillets will survive at higher resistances than those at which they were formed. This explains the difference between the downward and upward branches of the curve of Figure 8. The contaminant is spread again over the surface only to a small extent until the layer is thinned below the height of the fine structure.

The total amount of liquid on the surface can be estimated from the areas under curves such as those of Figures 2 and 3, making use of a mean observed rate of deposition obtained from the figures of Table 1 (4.4 \AA of layer per second per 0.1°C deviation). The area *DEFG* in Figure 2, formed by joining *G* and *D* by a straight line, corresponds to an addition of 90 \AA to the layer, which compares with a theoretical value of 60 \AA . It will be noticed that roughly as much liquid again is formed only to be absorbed by the fillets. In the step from 0.53 to $0.22 \text{ M}\Omega$ in Figure 3 the increase in layer thickness to produce the resistance change is again approximately as expected, but, as may be derived from the figure, about twice as much liquid is taken up by the fillets. The slow approach effects in this figure provide a basis for the estimation of the mean separation of the fillets. On account of a thinning of the layer in the proximity of each fillet, even an approximate calculation is, however, very difficult. On the doubtful assumption that the thinning may be neglected, a separation of the order of $6 \times 10^{-3} \text{ cm}$ is obtained.

The experiments throw some light on the fundamental question of the extent to which the vapour pressure of a very thin sheet of saturated solution on the surface differs from that of the bulk liquid. The temperature elevation at the higher resistances in Figure 3 cannot be regarded as being wholly a fundamental effect due to the thinness of the layer, because, as mentioned above, a few crystals showed very little temperature elevation even at a resistance of $10 \text{ M}\Omega$. The elevation shown in the figure has, in fact, already been attributed to general surface curvature. Figure 3 alone, in which the temperature elevation at $2 \text{ M}\Omega$

does not exceed 0.02°C , leads to the conclusion that the vapour pressure deficit of a layer approximately 80 \AA thick cannot exceed 0.15 per cent. Results less typical than those given in the figures indicate that even for a layer thickness of 40 \AA the intrinsic deficit is less than this amount.

Figures 6 and 7 show that even for a temperature deviation of 0.002°C a well-defined conductance drift occurs. The extreme sensitivity of the technique is apparent when it is realized that the rate of crystal growth or dissolution involved is one ionic layer per 5 min, corresponding to 1 mm in 30 years! Figure 7 also shows effects due to the necessity of establishing a definite supersaturation to obtain crystal growth on some regions of the surface and, indeed, effects representing an undersaturation necessary to obtain crystal dissolution in some regions. The growth resistance, at least, is only to be expected in view of Frank's (1949) mechanism of crystal growth.

If the large straight steps, present on the surface, are not parallel to a principal axis of the crystal, or if their faces are not perpendicular to the basal surface, they can support very easy crystal growth and dissolution at their faces, but in any case easy growth can occur at the bottom of each such step and easy dissolution at the top. In addition, growth can occur for a sufficient supersaturation, and dissolution for a sufficient undersaturation, at the steps which constitute the minimum fine structure, which is dislocation bound. The supersaturation at which the dislocation structure of any crystal can support prolonged growth depends on the number and distribution of dislocations which intercept the crystal surface; for crystals growing under ordinary conditions this may be regarded as being of the order of 0.1–1 per cent. It is, therefore, not surprising that secondary phenomena are revealed in Figure 7; the greatest supersaturation or undersaturation which could possibly have been produced at a given temperature deviation in those experiments is that which would have developed had the crystal failed entirely to grow (or dissolve), which is only about 2 per cent. for even the largest temperature deviations established (0.04°C). This value must be considerably larger than those which actually occurred. For a deviation from saturation in the solution of 1 per cent. the dislocation-anchored steps would, when straight, have to be no greater in length than about 2000 \AA and for a deviation of 0.1 per cent. no greater than $20,000 \text{ \AA}$. An estimated value of 4000 \AA for the spacing of the crests of the fine structure has already been given above. The behaviour for crystal growth would be expected to be as follows.

When a small temperature rise is imposed on the system the layer of solution will remain saturated in the neighbourhood of the high straight steps where it will consequently lose water to the vapour. If it is assumed that the steps are sufficiently widely spaced, the solution in regions between them will tend to become concentrated and to come into static equilibrium with the vapour. This tendency will be opposed by the diffusion of salt through the layer and by the viscous flow of the liquid under the influence of surface tension forces brought into effect by changes in the curvature of the free surface. On the other hand, the layer will tend to become non-uniform in thickness on account of the direct effect of surface tension differences which result from the small differences in

salt concentration. Liquid will tend to accumulate where the surface tension (and salt concentration) is greater. The author is indebted to Professor F. C. Frank (personal communication) for pointing out that the effect of such surface tension differences, even though in the experiments of Figure 7 they could not have exceeded about 1 part in 10^4 , would not be negligible on a clean surface. Frank has also pointed out that a contaminant which had spread on the surface of the saturated solution would resist the surface tension effect, not so much by reducing the surface tension as by constraining surface movement, and has thereby shed some light on the phenomenon of "seasoning" described in Appendix I. It will be argued below that the effect of surface tension differences may be neglected for "seasoned" crystal elements. In curves such as those of Figure 7 the rate of change of conductance will increase at first more or less linearly with temperature deviation, while remaining less than that corresponding to the reference line on account of the resistance mechanisms of diffusion and viscous flow. As the temperature deviation is further increased and new nucleation sites become active, the curve will bend back towards the reference line and, in accordance with the theory of crystal growth, will eventually become coincident with that line. A corresponding behaviour would be expected for crystal dissolution.

Generally speaking, the curves in Figure 7 show this behaviour but possess individual features. They all show the effect of a growth resistance, but, except for case (c), the growth branches do not appear to return to the reference line at high rates, but become parallel to that line. Presumably they would have returned had it been feasible to extend the experiments to higher rates and to allow protracted growth to occur. Curves (b) and (d) plainly show effects due to a dissolution resistance, while curve (a) shows only a small effect. In this curve and in curve (c), where no dissolution resistance is in evidence, the slope of the curve approximates that of the reference line as the origin is approached. This indicates that, in these cases, the initial fine structure contained features unable to resist dissolution and unable to resist a small amount of growth. In the growth branch of (a), as the temperature deviation increases from zero, the rate increases more and more slowly with deviation until, at about 10^{-2} °C deviation, a new mechanism abruptly comes in. The diminishing slope presumably indicates that features which initially supported easy growth at sites between the high steps were being progressively exhausted as the experiment continued.

Even in curves (b) and (d) continuity of slope exists at the origin. This is consistent with easy growth and easy dissolution occurring at the same places; it at least requires the average separation of the sites of easy growth to be the same as that of the sites of easy dissolution. The average separation can be estimated from the difference of the slopes of curves (b) and (d) and the corresponding reference lines at the origin. Calculations in which the preponderating mechanism is assumed to be salt diffusion on the one hand, and viscous flow due to local differences in surface curvature on the other, give values for the mean separation respectively of the order of 10^{-2} and 10^{-3} cm. If an analogous calculation is made for viscous flow under the influence of surface tension

differences a distance is obtained which is about double that obtained from the calculation based on salt diffusion. The effect will not predominate, however, because the crystal elements were "seasoned" and the experiments of Appendix I must be interpreted as showing that seasoning greatly reduces the role played by surface tension differences; the effect may justifiably be neglected. The principal transport mechanism is, therefore, that of salt diffusion and the derived separation of 10^{-2} cm is seen to compare favourably with the tentative estimate given earlier for the separation of the large liquid fillets, and the spacing of the steps observed by Amelinckx (1951).

The small counter-drift effect, which in some circumstances follows a rapid drift in conductance and which has been described above, may be explained as arising from the tendency of the step structure to "run back", eliminating any marked curvature which has been developed; some contribution to the effect, however, may be made by the influence of the liquid fillets.

(c) *The Significance of the Results for the Hygrometer*

When the automatic hygrometer is operated in a normal manner the crystal resistance is maintained at an almost constant value. The performance obtained depends on the closeness with which the balance temperature T approaches the equilibrium temperature T_e and the way in which the resistance changes when small deviations of the temperature occur.

It has been seen that the temperatures T and T_e agree within 0.01 °C for resistances from 0.1 to 1 or 2 M Ω and that towards the upper end of this range this accuracy of agreement is attained very rapidly, even when a considerable change in the resistance is made. With some individual crystals close agreement extends to rather higher resistances.

The results show that an automatic hygrometer can measure a change in humidity with an accuracy of 0.002 °C or better in the equilibrium temperature (or in the dew-point). This is proved in a direct way by Figure 5. Also, it is clear that there is no effective fundamental limit to the speed of response attainable with the automatic form of the hygrometer. In practice the speed is limited by aspects of heat flow. However, if the humidity is varying more rapidly than the apparatus can accommodate, and the resistance of the crystal element is changing markedly, memory effects become significant and transient errors other than those due directly to the finite response time of the control system occur. These errors are unlikely to exceed 0.1 °C. In practice, the rate of change of humidity of the incoming gas can easily be limited to a level with which any particular system can cope simply by inserting in the gas line a dead volume of suitable magnitude within which mixing can occur. The overall response time may still be only a few seconds.

The equilibrium temperature has been shown to be independent of the rate of flow of the gas over a considerable range. It should be noted, however, that extremely low rates of flow are objectionable for several reasons and that, of course, there exists an upper limit beyond which the inlet heat exchanger becomes inefficient.

The ideal of a linear relationship between the rate of change of conductance and the temperature deviation is approached closely with crystals the surfaces of which have been formed by cleavage, as has been shown. The deviations from linearity which are apparent in Figure 7 are of little practical importance for the hygrometer. Probably, with the use of crystals the surfaces of which are formed deliberately at a small angle to the (100)-like planes, the rate curves can be made quite straight. Of the fine and coarse structures of the surfaces, the former must be regarded as fundamental, although conditions of manufacture can probably be found which minimize the initial height of that structure. There is no reason, on the other hand, why the coarse structure should not be practically levelled by a suitable technique. However, to gain the full potential advantage of doing so, the electrode edges would have to be feathered or rendered unwettable by the solution. Feathering of gold electrodes could easily be accomplished by spacing the mask from the surface during vacuum evaporation. These refinements may be worth while for some research applications of the technique.

As Figure 8 illustrates, the resistance-temperature plot in the presence of soluble contamination is approximately linear except at high resistances and the line extrapolates closely to the temperature T_c at zero resistance. The fact that the plots for downward and for upward resistance steps are different means that a regular resistance sequence is necessary when extrapolation is contemplated. A downward resistance sequence is to be preferred. In practice contamination is not a serious problem under ordinary conditions. The almost complete lack of effect of an oily contaminant is a striking feature. Clearly, a monolayer of oleic acid offers little additional resistance to the transfer of water vapour. The vapour diffuses through the monolayer and dissolves the crystal reversibly at its true surface, "floating" the monolayer off. It should be pointed out that, even if a surface contaminant were to offer a considerable diffusion barrier, there would be no consequent limitation on either the accuracy or *speed of response* of the hygrometer, since the effect is wholly compensated if the gain in the control system is increased sufficiently, the water-storage capacity of the monolayer being negligible. In fact, if the evaporation process is hindered appreciably, the design of the control system is facilitated, as will be shown elsewhere.

The effect of temperature on the detailed properties of the crystal element has not yet been specifically investigated. It is inherent in the above theory that the effect will be due mainly to the influence of temperature on the sensitivity factor J , tabulated in the previous paper, and on the viscosity of the saturated solution. The effect of temperature on surface tension is relatively quite small. The slow recovery effects exemplified in Figure 3 are the net result of the competing effects of surface flow, which is governed by surface tension and viscosity, and of the continuous transfer of water vapour to or from the surface, which, as far as the consequent temperature errors at constant resistance are concerned, is governed by J . The magnitude of this slow transient may, therefore, be expected to be a function of the product of J and the viscosity. However, the temperature dependence of J is considerably larger than that of

the viscosity so that for a rise of equilibrium temperature of, say 10 °C, a considerable reduction of the slow transient may be expected. General experience indicates that such is the case.

VI. CONCLUSION

It has been shown that potassium chloride crystal elements, end-coated as described, possess sharply defined properties with respect to water vapour. These properties are favourable for hygrometric purposes.

The secondary effects evident in Figure 3 and the energy barrier phenomena evident in Figure 7 are deserving of a more complete quantitative analysis than has yet been made. However, to be really useful such an analysis must be based on a knowledge of the actual structure of the surface of the crystal. The coarse structure can probably be determined by multiple-beam interferometry or phase contrast techniques but the fine structure may be beyond the reach of such methods. Also, the difficult problem of determining the transient viscous flow which occurs in a very thin liquid layer under the influence of surface tension forces requires detailed investigation.

In future work it is hoped to extend the experiments to other crystal substances and temperatures and to attempt a correlation of the surface structure, as determined by direct means, with the observed behaviour of the crystal elements.

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APPENDIX I

Observations made with potassium chloride crystals of analytical reagent purity reveal some interesting and easily observed properties of the freshly prepared surface with respect to water. The following experiments were performed in an air-conditioned room at a temperature of 20 °C and a relative humidity of approximately 50 per cent.

If a surface freshly formed by cleavage is breathed on lightly through a short length of tube the surface becomes covered by a large number of tiny droplets which presumably consist of saturated solution. If the droplets are allowed to evaporate and the experiment immediately repeated the result is the same. A sustained breath gives rise to large droplets of liquid, perhaps 0.1 mm

in diameter. These not only do not spread on the surface but may be moved bodily over it. The contact angle is relatively large. If a droplet is forcibly spread to cover an appreciably increased area, its edge retracts when the deforming force is removed and roughly the original form is resumed. If a freshly cleft surface is completely flooded two or three times using the breath copiously, a subsequent light breath produces film-wise dissolution of the surface and interference colours are observed.

Thereafter only film-wise dissolution is observed even if a monolayer of oleic acid is laid down on the crystal surface. In fact, using a microscope, no difference in behaviour is observed between "seasoned" surfaces which do and those which do not possess an oleic acid layer. Oleic acid is easily shown to spread strongly on the saturated solution.

The ease with which a cleft surface can be flooded and induced to form surface films depends on its age. Surfaces which have been exposed to the atmosphere for several hours are already practically "seasoned", being flooded readily by a light breath. Seasoning of the surface by dissolution and regrowth is also desirable after washing away a marginal layer of the crystal in pure methanol and drying with filter paper, the freshly washed surface behaving in much the same way as one freshly produced by cleavage.

Droplets of the saturated solution applied to a clean, dry crystal surface have never been observed to spread spontaneously over the whole surface but settle down with at least a small but easily observed angle of contact. However, provided the surface is not freshly prepared, the liquid, if pushed over the surface, shows no tendency to retract at its edge. Also, if a discrete drop is present on the surface and a continuous layer is formed on the remainder of the surface by breathing on it, the drop spreads over the surface.

Following on suggestions by Frank (personal communication) that the effects of surface tension differences are significant, and that seasoning consists in the acquisition of minute quantities of surface-active material from the atmosphere, some experiments were performed in which it was found that a crystal behaves alternately as a seasoned and as an unseasoned crystal when washed alternately in methanol containing about 0.1 per cent. of oleic acid and in pure methanol. Also a droplet of saturated solution on a fresh surface, if touched with a fibre coated with oleic acid, spreads over the surface at a light breath and the surface is then found to be in the seasoned state.

There is little doubt, therefore, that seasoning represents the acquisition of traces of a surface-active substance. It is proposed to investigate these phenomena systematically at a later date.