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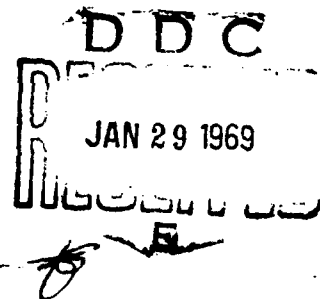
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The growth of condensation nuclei with relative humidity.

by C. Junge.

1. Growth at medium humidity.

Various observations of natural aerosol point to the growth of nuclei with relative humidity. The decrease in visibility with increased humidity is particularly instructive (18, 19, 20). Since aerial turbidness is almost exclusively caused by particles with a radius larger than 10^{-5} cm, the change in visibility reflects the growth of these nuclei. Another factor depending on the nuclear radius is the relation P of neutral nuclei to charged nuclei. On the basis of theoretical considerations, Wright (17) found the following values, if only the presence of particles of equal size is considered:

Radius =	1	2	4	6	∞	X 10^{-6} cm
P =	10	3.3	2.0	1.7	1.5	

Thus P applies practically only to a size change of particles with a radius smaller than about 10^{-5} cm, provided we assume that Wright's calculations remain applicable also to very complex spectra of nuclear sizes. Visibility and the relation P together give a clue to nuclear growth with humidity in the whole range of condensation nuclei from ca. 10^{-6} to $5 \cdot 10^{-5}$ cm.

Direct measurements of nuclear sizes with increasing humidity — perhaps by the determination of ionic spectra according to Israel (7) — are very difficult because the natural ionic spectra are not sufficiently "monochromatic" to allow positive observations of the growth of a characteristic group of nuclear sizes. Different types of nuclei, e.g. those produced by gas flames, show a uniform size only immediately after their formation. However, this size is still below r = 10^{-6} cm, since commonly all types of combustion nuclei commence to grow only after their genesis, and then only due to coagulation.

Fig. 1 depicts a few typical observations of the sizes mentioned. The growth of nuclei evidently sets in at about 70% relative humidity and increases upon approaching saturation. As this growth characteristic seems to coincide in various nuclear size ranges, we are apparently dealing here with a generally valid law of the atmospheric aerosol. So much for the observations; what about their interpretation?

As is well known, Koehler has first pointed to the growth of solutional droplets with humidity. Fig. 2 represents curves calculated according to his process, on the basis of generalized formulae (12) proceeding from the nuclear radius at 100%, which Linke designates as the potential nuclear radius, and ignoring the changes in surface tension

and other factors with the concentration . They reflect quite
satisfactorily the quality and, as demonstrated by Wright (18), the
quantity of visibility loss or increase in turbidness with growing
humidity above ca. 70%. However, below this degree of humidity
calculations and observations do not agree, which cannot be attributed
to the indicated simplifications in the computation, as is easily shown.
Wright (19) suggested the possibility of crystallization of the dissolved
substance. Under the condition defended by him, that nuclei close to
the oceans consist predominantly of sodium chloride, this crystallization
would indeed set in between 60 and 70%. Simpson (14) correctly points
out that crystallization is an unstable process, since the vapor pressure
depression of the continually saturated solution remains the same, while
the vapor pressure elevation increases due to the curvature of the
nuclear surface. Once started, crystallization continues until all of
the solution's water is completely evaporated. This would mean a sudden
diminuation of the radius by about 50%. In addition, according to
Dessens' observations (4,5) of vapor droplets with r greater than 10^{-5},
strong supersaturation of the solutions may take place before evaporation
occurs, which then is very vigorous, however.

Either one assumes a growth according to the computed curves in the
case of pure solutional droplets or a sudden alteration, both in contra-
diction to the facts. Therefore an explanation shall be attempted here
which proceeds from the consideration that a vigorous coagulation of the
particles sets in, particularly in smokes, combustion gases and in large
cities generally, and that a large part of the nuclei represent mixed
nuclei which contain partly soluble, partly insoluble substances. When
the growth of such nuclei is calculated, the curves depicted in Fig. 2
are obtained, which proceeded from the same potential nuclear radius as
in the case of pure solutional droplets, and where the radius of the
solid portion of the substance is indicated. It is evident that below
ca. 70% the solid portions are enveloped only by a relatively thin
solutional membrance, and that the particle's radius barely changes; a
more or less strongly pronounced growth occurs in diverse fashion only
above this degree of humidity. The best qualitative agreement with the
visibility, etc. is offered by curve 8, where the radius of the solid
portion of the substance amounts to 20% of the potential nuclear radius.
It should also be pointed out that, according to Wall, nuclear growth
becomes decisive only below r = 10^{-6} due to the adsorption of mono or
multimolecular water layers on solid nuclear surfaces, as suggested by
curve 2 in Fig. 2 (16).

The computation of curves for mixed nuclei was conducted with the
aid of formulae valid for pure solutional droplets. According to
Linke (12), the following is applicable to the latter:

$$100-F = \frac{Q}{r^3} - \frac{1.13 \cdot 10^{-5}}{r} , \quad (F= \text{relative humidity, } r= \text{nuclear radius}),$$

where the constant Q becomes Q = $1.13 \cdot 10^{-5} \cdot r_1^2$ through the radius r_1

of the nucleus at $F = 100\%$ (potential radius). Accordingly, the following is obtained for a mixed droplet:

$$100-F = \frac{Q}{r^3 - r_o^3} - \frac{1.13 \cdot 10^{-5}}{r} ,$$

where r_o designates the radius of the solid portion of the substance and Q becomes $\quad Q = \frac{1.13 \cdot 10^{-5} (r_1^3 - r_o^3)}{r_1} .$

It should follow from these considerations that mixed nuclei predominate in most aerosols. This matter cannot be decided at this time since the correlations of visibility and the P-value with humidity statistically arrived at in Fig. 1 may be affected by the following additional factors:

1. In the classification of the observation results according to humidity, a selection of aerosols could have taken place at the same time, in the sense that the atmospheric substances with a higher humidity may, according to their origin, contain aerosols with larger particles or larger quantities of particles, due to the geographical location of the test site. Still, the probability of such a selection is small, especially since the curves of Fig. 1 are being confirmed from diverse quarters.

2. By an effect of higher relative humidity which promotes coagulation.

Before the second point is treated in more detail, a few remarks concerning the present status of the metric-technical treatment of aerosols should be interpolated. The entire range of aerosol particles of meteorological interest covers radii of about $5 \cdot 10^{-7}$ to 10^{-4} cm. Basically, all these particles should be counted by the nucleus counter. Whether this is the case is not positively known; it is possible that the limit of the small particles varies in the individual instruments according to the conditions of expansion utilized, that on the other hand particles with a radius larger than $2 \cdot 10^{-5}$ grow, corresponding to Fig. 2, so strongly in the saturated air of the cloud chamber that part of them precipitate out prior to measurement. This is indicated by pictures of condensation nuclei under the electron microscope, as described by Linke (13). Perhaps this explains the inconsistency found by Israel and Krestan (8) upon comparing several nucleus counters. Parallel to the nucleus counter, the larger particles with a radius of 10^{-5} are detected by the dust counters, apparently owing to the type of metric method, but this is essentially true only of solid particles. As Dessens has recently demonstrated, droplets in this size range are far more numerous than solid particles; he finds several hundred droplets in clean rural air, while the dust count under the same conditions amounts to between ten and hundred.

No matter how the metric ranges of these diverse methods may
compare, in any case the measured quantity of particles cannot be
affected by the relative humidity of the tested air in connection with
all methods. If, therefore, observations (6,11) show in close agreement
that the number of nuclei decreases with growing humidity and the number
of dust particles rises, the conclusion suggests itself that humidity
exerts an influence favorable to coagulation. According to the concept
of the coagulational process (15), well supported by tests, it is
practically independent of the particles' size. Therefore the growth of
particles with humidity ought not to effect an acceleration of coagula-
tion, if the rule is strictly valid that every type of contact produces
fusion. This is certainly the case with droplets, but need not apply to
solid particles. It is conceivable, therefore, that the absorption of
water by the nuclei evidently taking place at 70% relative humidity
produces a higher effective degree of coagulation, and thus explains
the observations.

These considerations will show how difficult it is to give precise
data on the growth of condensation nuclei at medium humidity. The
individual effects should be studied separately in extensive laboratory
research.

2. Growth at high humidity.

The behavior of condensation nuclei above 90% relative humidity
shows peculiarities that deserve detailed examination. The most
important phenomenon in this connection is the occurrence of socalled
dry fogs which frequently are found not only in densely populated areas
and industrial complexes but also on the ocean and which heretofore have
generally been considered as a proof for the presence of very hygro-
scopic condensation nuclei. A few observations are listed in the
following table, according to Ashmore (2):

Location; number of cases		100 -99	98 -97	96 -94	93 -90	<90	% relative humidity
Cardington	124	28	44	16	9	2	all fogs;
Eskdalemuir	143	45	36	16	3	0	visibility below 200 m
Grayshott	191	85	11	1	2	1	
Cardington	34	44	32	12	12	0	dense fog;
Eskdalemuir	52	44	33	19	4	0	visibility below 100 m
Grayshott	54	96	4	0	0	0	

Frequency of dry fogs at several English stations in %, according to
Ashmore (2).

Their most important result is that the dry fogs suddenly become
quite frequent above 97%, and that this frequency decreases rapidly
between 90 and 97%. They are rare below 90%.

A glance at Fig. 2 makes it plausible that the incidence rises above

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96% due to the vigorous growth of the fog droplets. Local differences in the course of incidence may be explained by divergent average nuclear sizes; Eskdalemuir and Cardington would have larger average fog droplets than Grayshott. However, the rapid abatement of frequency below a certain humidity remains peculiar to all three localities, a circumstance that is difficult to explain by means of the growth curves; since according to them abatement should take place more slowly and -- depending on the aerosol -- dry fogs should appear at considerably lower humidity. One. could again consider the possibility of preferred selection of weather conditions with copious nuclei in connection with especially high humidity, as well as an increasing effect of coagulation. In the following, attention will be directed to the hitherto neglected effect of trace gases on nuclear growth, which may perhaps be held responsible for many a dry fog.

A number of trace substances of the air are more or less volatile. Part of these gases are absorbed (dissolved) by the existing nuclear droplets and maintain a vapor pressure equilibrium with the gas phase at a certain solutional concentration. Due to the small volume occupied by the total amount of condensation nuclei in the space unit air, an essential portion of the total substance is dissolved only in the case of poorly volatile substances, such as HCl, HNO_3 and H_2SO_4; in gases such as SO_2, NH_3 this portion is infinitesimal compared to the amount present in the gas phase.

Fig. 3 treats this subject in more detail. Curve 2a shows the growth of a normal solutional droplet. An HCl partial pressure of $23.2 \cdot 10^{-6}$ is assumed, corresponding to $50 \cdot 10^{-6}$ g/m^3 trace substance. This is the size category of chloride traces found at various locales above the continent (3), although a large portion of chloride is present in the form of salt. The computations were based on HCl solely because it is known to have partial pressures over aqueous solutions down to 10^{-4} mm Hg and therefore permits a fairly certain extrapolation to even lower values. The presence in the atmosphere of H_2SO_4 and HNO_3 nuclei is far more probable; unfortunately the pertinent tabulations do not contain such values for them. Basically the same curves should result as in the case of HCl, with the exception that the critical growth humidity discussed below will differ according to the peculiarities of the substances; it ought to be considerably lower in the case of H_2SO_4 which is of particularly poor volatility.

In the event of the assumed partial pressure of HCl, only one part is dissolved in the nuclear droplet, so that its radius grows by a trifle, expressing itself by a small deviation to the right. If the humidity continues to go up, at 97% the vapor pressure depression is achieved which corresponds to the HCl solution in equilibrium with the gas partial pressure. Upon further humidity elevation an increased absorption of HCl must set in, leading to a strong growth of the fog droplet, which persists until the partial pressure diminishes perceptibly. When this critical humidity is exceeded, the growth of nuclei abates, since now the major portion of HCl is already in solution.

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In the computation, the total amount of HCl was divided into the gas phase and the dissolved phase. The appropriate partial pressure can be established from the amount of gas, leading to the determination of the balanced solutional concentration and the equilibrial humidity. The size of the nucleus can then be computed from the solutional concentration and the amount of HCl dissolved in the nucleus by equating the density with 1 (see the table on p. 134).

The relation between vapor pressure depression and nuclear radius thus arrived at is shown by curve 1 (Fig. 3); subtracting this curve from 2a gives us the humidity-radius curve of a solutional droplet in the presence of a partial gas pressure. Curves 3a, 3b show the same for larger solutional droplets. It is evident that only the large nuclei can participate in growth, since the smaller ones have a higher critical humidity (K). In order to gain an idea as to how curve 1 in Fig. 3 would change when different amounts of nuclei take part in growth, or when different quantities of trace substances are present, Fig. 4 has been included. Since the more recent investigations by Dessens indicate that approximately 300 fog droplets per cm^3 of 1 to $5 \cdot 10^{-5}$ cm size must be expected even in clean rural air, the curves computed for this number of nuclei must be considered to be the most probable; i.e. the droplets, after reaching the critical humidity, continue to grow to about $2 \cdot 10^{-4}$ cm and their size subsequently changes relatively little up to saturation, which makes the great stability of many dry fogs plausible.

According to the concepts advanced here, the size of the nuclei is dependent upon the humidity and the gas partial pressure. Depression of the gas partial pressure causes a decrease in nuclear size even at constant humidity. Fog droplets consisting solely of HCl, etc. may disappear completely in this case. Upon admixture of air from industrial areas to clean air, all poorly volatile substances gradually change over into the gas phase, the aerosol is purified and there remain either solid particles or solutional droplets of non-volatile substances, primarily salts. When such air condenses, the partial pressure conditions change considerably. If the amount of water present in saturated air in liquid form is assumed to be 10^4 times greater, the major portion of poorly volatile substances and a considerable part of more readily volatile gases is absorbed by the cloud elements and then returns to earth with the rain. The formation of clouds and rain purify the atmosphere of gaseous components. It follows that chemical analysis of precipitation may not be used for inference as to the substances of nuclei responsible for condensation, especially since, in addition to gas traces, many condensation nuclei will be deposited on the droplet.

In the presence of SO_2 which is found almost entirely in the gas phase, the following may occur: By oxidation to SO_3, either through ozone or through photochemical processes and deposit of water to form H_2SO_4, the major part of the substance is now absorbed by the extant nuclei, which grow correspondingly. As demonstrated by Aitken (1), the appearance of dry fogs after sunset is often characteristic of industrial areas. Aitken attributes this to the formation of new condensation nuclei

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due to oxidation of SO_2, which certainly may be a factor in addition to the growth of already present nuclei.

In closing, the speed at which the equilibrium between gas partial pressure and solution is achieved shall be discussed briefly. The kinetic gas theory allows the computation of the number of gas molecules impinging upon the surface of a nucleus with a radius of $r = 10^{-5}$ per second. At an HCl partial pressure of 10^{-5} mm Hg and a temperature of $10°C$ this amount equals $2.6 \cdot 10^{-16}$ g/sec, i.e. about $4.4 \cdot 10^{6}$ molecules HCl. At 2% weight concentration of HCl a nucleus contains $8.4 \cdot 10^{-17}$ g or $1.4 \cdot 10^{6}$ molecules HCl. Thus, in one second, three times as many HCl molecules strike the surface as are contained in the nucleus, i.e. the rate of balance achievement will be of the magnitude 1 second. In clouds the rate of equilibrium will be considerably faster, since the gas concentration is lower here and the content of dissolved substance higher.
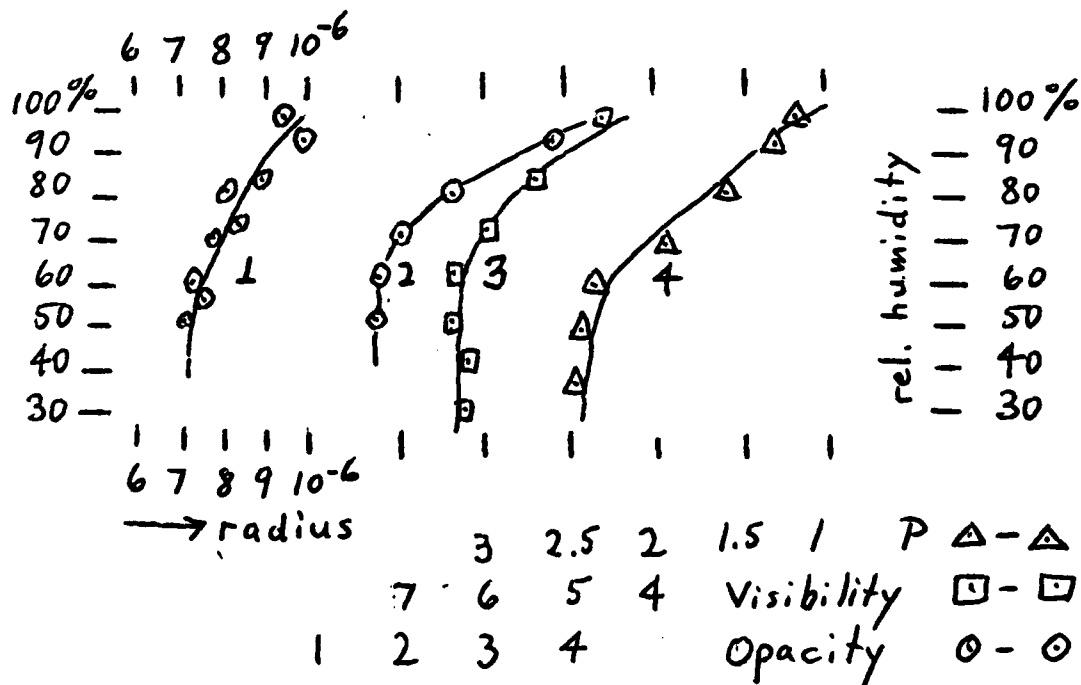

Fig. 1. Observations of nuclear growth with relative humidity.
Curve 1: Measured growth of newly created gas flame ions according to (10).
Curve 2: Dependence of opacity upon humidity according to (19).
Curve 3: Dependence of visibility upon humidity according to (10).
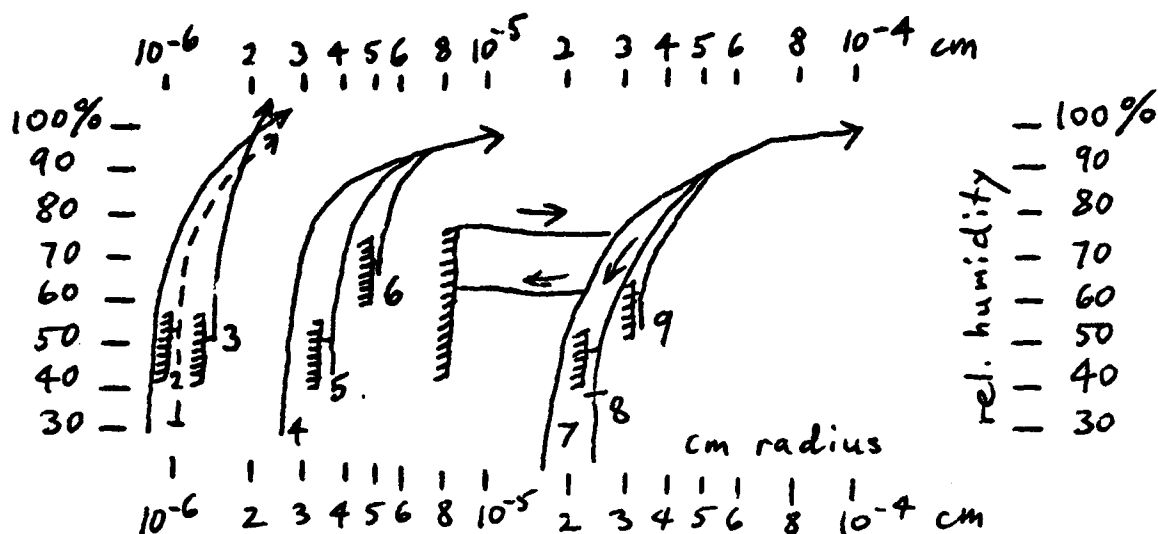Curve 4: Dependence of P upon humidity according to (9).

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Fig. 2. Growth curves of condensation nuclei.
Curve 1,4,7: Pure solutional droplets with a potential nuclear radius of
$2 \cdot 10^{-6}$, 10^{-5} and 10^{-4} cm. The process of crystallization
and re-dissolution is indicated schematically on curve 7.
Curve 2: Growth of a solid nucleus with a radius of 10^{-6} cm and the
surface properties of glass owing to adsorption according to (16).
Curve 3,5,6,8,9: Growth of mixed nuclei with different radii of the solid
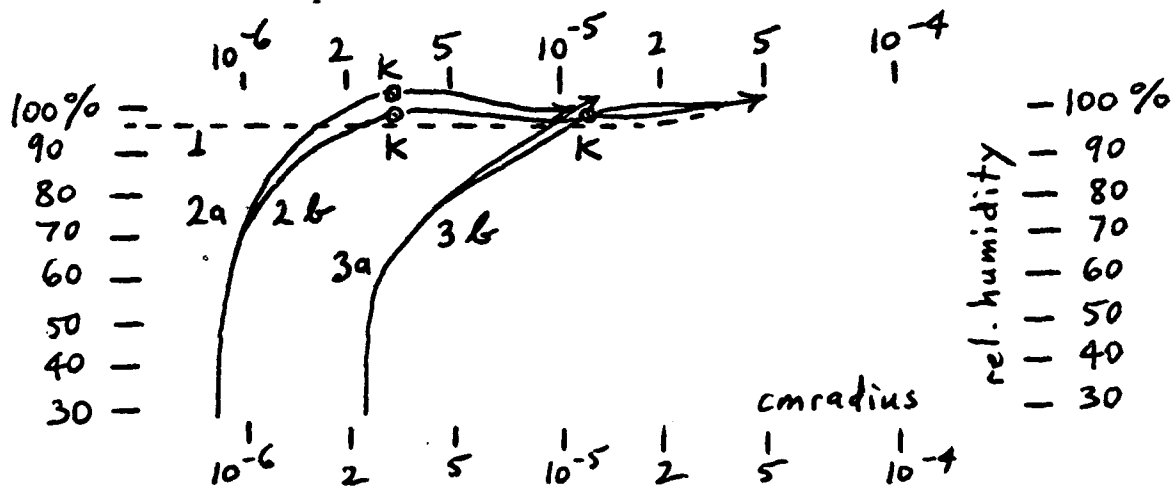portion of the substance.

Fig. 3. Change in the growth curves of nuclei in the presence of
poorly volatile substances.
Curve 1: Relation between vapor pressure depression due to absorption and
nuclear radius in connection with a known amount of a poorly
volatile substance.
Curve 2a,3a: Normal growth of solutional droplets.
Curve 2b,3b: Same growth curves in the presence of poorly volatile subst.
K: indicates the humidity at which condensation sets in (critical humidity).

HCl dissolved in nuclei	0	5	15	30	45	$\times 10^{-12}$ gr/cm^3
HCl in gaseous form	50	45	35	20	5	$\times 10^{-12}$ gr/cm^3
Partial pressure HCl	23	21	16	9	2.3	$\times 10^{-6}$ mm Hg
Solutional concentration	2.5	2.4	2.2	1.6	0.6	weight percentages
Relative humidity	97	97	97.5	98	99.3	%
Total weight of nuclei	0	2.08	2.3	3.1	8.3	$\times 10^{-10}$ gr/cm^3
Radius of droplets	0	1.70	1.76	1.95	2.71	$\times 10^{-5}$ cm

Total HCl: $50 \cdot 10^{12}$ gr/cm^3
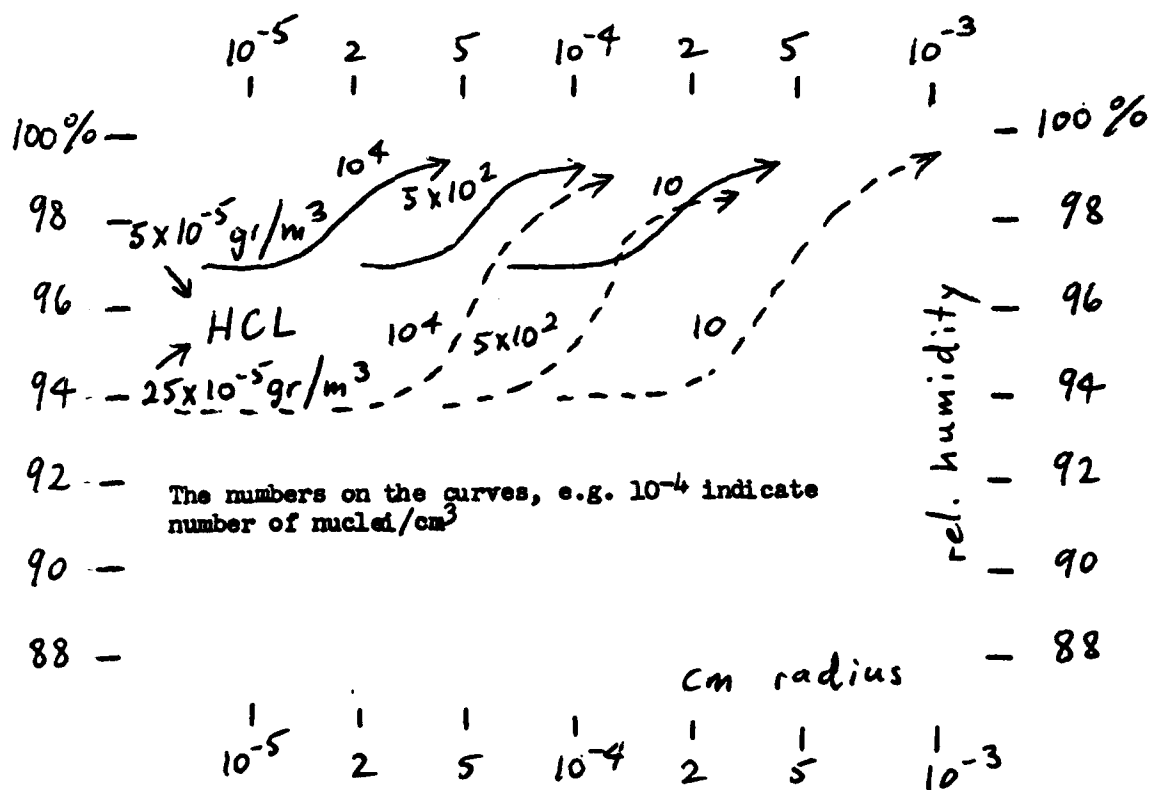Number of nuclei participating in growth: 10^4 per cm^3.

Fig. 4. Relation between vapor pressure depression due to absorption and nuclear radius under the assumption of different quantities of HCl and nuclei taking part in growth.