Supersaturation Effects on the Change

of Phase in the Equilibrium

Solid ↔ Solid + Gas

by

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May 25, 1953

Signature of Author: _____

Signature of Thesis Supervisor: _____

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Dept. of Chemical Engineering
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Cambridge 39, Massachusetts
May 25, 1953

Secretary of the Faculty
Mass. Institute of Technology
Cambridge 39, Massachusetts

Dear Sir:

The thesis entitled "Supersaturation Effects on the Change
of Phase in the Equilibrium; Solid $\rightleftharpoons$ Solid + Gas" is
hereby submitted in partial fulfillment of the requirements
for the degree of Bachelor of Science in Chemical Engineer-
ing.

Respectfully submitted,

Signature redacted

Donald E. Pickles

## Acknowledgements

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# Plots and Illustrations

## Summary

This thesis is a study of the effect of supersaturation upon the rate of reaction of the type, Solid → Solid + Gas. After preliminary investigation, attention was focused upon the development of supersaturation in the reaction $Na_2SO_4.10H_2O \rightarrow Na_2SO_4 + 10 H_2O$. This material was chosen because there was only one possible solid product of reaction and because a measurable amount of gaseous product was present at equilibrium at room temperature.

Three different experimental procedures were used.

The first was carried out to find the degree of supersaturation obtainable (i.e., the degree to which the vapor pressure of water over $Na_2SO_4.10H_2O$ could be lowered below equilibrium without reaction occuring.) A crystal of the decahydrate was placed in a flask surrounded by a constant temperature bath, and the pressure over the crystal was very slowly reduced. Temperature gradients through the crystal and the walls of the flask were considered negligible, and the temperature at the reaction zone on the crystal surface was taken as that of the constant temperature bath. Working with this system, the crystals were found to start to decompose from 1.5 to 4.0 mm. (Hg) below that corresponding to the equilibrium vapor pressure at bath temperature.

Some doubt arose as to the validity of the assumptions that the temperature gradients through the crystals and flask were negligible. To obtain a more accurate reaction zone temperature, the decahydrate crystals were grown around the bulb of a thermometer. The assumption was made that the heat flow necessary for the reaction would be through the gas surrounding the crystal

and not through the crystal beneath the zone of decomposition.
Thus the thermometer would give the temperature of the reaction
zone. This system showed much less tendency to have a lower
water vapor pressure over the crystal than that corresponding
to the equilibrium pressure at the temperature read on the
thermometer.

The results of a fluidized bed procedure were similar. A
bed of the finely divided decahydrate was fluidized by passing
air through it. The vapor pressure of the water in the effluent
air (measured by wet and dry bulb temperature readings) was
initially very close to the corresponding equilibrium pressure
at the bed temperature. However, as decomposition of the bed
proceeded, the exit vapor pressure tended to go noticeably
lower than the bed temperature equilibrium pressure. This might
be explained by formation of a coating of anhydrous sulfate
around each particle of the decahydrate. This coating could
have acted as insulation by preventing the flow of heat to the
reaction zone where the decahydrate was decomposing, or it
could have acted as a barrier through which the water vapor
evolved had difficulty diffusing. Also, with the formation of
this anhydrous coating, there would be a decrease in the volume
of each decahydrate particle and a corresponding decrease in
the area of the surface of these particles. Thus, area of the
reaction surface might be a factor in governing the reaction.

Using a similar fluidized bed technique (but using hot $N_2$
instead of air as a fluidizing medium) Lindal (5) found that
low partial pressures of $CO_2$ could be obtained with the decompo
sition of a bed of $CaCO_3$. In fact the pressure was only half
that corresponding to the bed temperature. This seems to indicate

that $CO_2$ is held to CaO much more strongly than $H_2O$ is held to $Na_2SO_4$. The answer to this may be that the first is a case of strong electron-sharing bonds whereas the second is a case of weaker Van der Waals forces.

Interpretation of the results is clouded by the fact that current work in the laboratory (Glass) indicates that a large part of the gas rising through a fluidized bed comes in to little contact with the solid particles in it. In consequence, one can think of some of the gas as practically completely bypassing the solids in its flow through the bed. However, this seems untenable in the light of the fact that in the early stages of the run in Figure 4 the out going gas is so very nearly in equilibrium with the solids in the bed. In that run the tendency of the out going gas to be farther from equilibrium as time went on is unmistakable, despite the fact that this failure to continue to reach equilibrium develops when only about one-quarter of the original decahydrate has decomposed. This is in contradistinction to the experience of Lindal who found the same fraction of equilibrium attained up to over 80% decomposition of his calcium carbonate. Despite the uncertainties, it seems indicated (1) that the gas initially approaches equilibrium with the decahydrate very closely indeed, whereas calcium carbonate, with approximately the same degree of contact between solids and gas, comes only about half way to equilibrium, but that (2) the rate of decomposition of the deca-hydrate begins to drop off at far lower percentage decomposition of the solid as compared with the behavior of the carbonate. These differences apparently stem from fundamental differences in the behavior of the two solids rather than differences in the character of the contact between gas and solids in the two cases.

## Introduction

The phenomenon called supersaturation - saturation beyond equilibrium has been observed in many forms for many years. The sugar industry has used supersaturated solutions to crystalize sugar for years. Glass is a supercooled material - far below the equilibrium temperature at which it should crystalize - at room temperature. Hydrated salt crystals have been known to stay transparent and unchanged for years at room temperature and atmospheric conditions whereas data on dissociation pressures indicate that they should have effloresced (1). Certain salt crystallization processes use supersaturated solutions in which to grow the crystals (2).

Much literature has been written on the kinetics of reactions under supersatured conditions (8). General agreement has been reached as to the process by which these conditions are relieved, the process being called nucleation and defined as "the generation of, within (upon) a metastable phase, then initial fragments of a new and more stable phase capable of developing into the gross fragments of the more stable phase" (3).

Unfortunately, the literature contains little clear and pertinent data, especially concerning the reaction: Solid ↔ Solid + Gas. However, several things may be deduced which have helped in my study.

(1) Supersaturated phases reduce their energy and approach equilibrium by the nucleation and growth of a new phase. (13)(10)

(2) Nucleation of a new phase upon a solid phase takes place at active centers or imperfections on the solid phase. (12)

(3)  Reaction of the type under study take place at the interface between the solids.  (7) (9) (4)

(4)  In certain specific cases, the reaction zone at the interface moves from the surface inward at a constant linear rate.  (7) (12)

Lindal (5) fluidized a bed of $CaCO_3$ with nitrogen at high enough temperature to decompose the carbonate.  When a plot was made of the $P/P_e$ (P was observed pressure of the $CO_2$ given off and $P_e$ was the dissociation pressure of the carbonate at the bed temperature) against the fraction decomposed, a straight line at $P/P_e$ equal to 0.5 was obtained until the carbonate was depleted at 0.9 decomposed.  Thus the actual pressure was only 0.5 the equilibrium pressure for the observed temperature.  This demonstrates that the material was superheated and some distance from equilibrium.

Similarly, in this thesis a bed of $Na_2SO_4.10H_2O$ was fluidized with air and the effluent water vapor pressure measured and compared to the bed temperature equilibrium pressure.  This technique was used because it gave a constant mixing, even temperature reaction zone, in which localized heat flow and supersaturation was cut to a minimum, and the temperature at the reaction zone was found easily and accurately.

Also, the degree of supersaturation of the decahydrate obtainable in a fixed bed was found.

## Procedure I

A boiling saturated solution of sodium sulfate was
filtered and put into a 600 cc. round bottom flask. It was
then cooled to 30°C. and "seeded" with a small crystal of
$Na_2SO_4.10H_2O$. By letting the seed grow overnight, a
crystal of considerable size was obtained (about 100 gm.).
The excess mother liquor was poured off as far as practicable.
The flask was returned to a vertical position, placed in a
water bath (the temperature of which was measured carefully),
a two-hole rubber stopper inserted, and the pressure over the
crystal was slowly reduced. The apparatus used is shown in
Figure I. A series of condenser and dry ice-acetone traps
insured even pumping rates to low water vapor pressures. The
pressure was read at various times on a manometer which was
attached to the reaction flask.

Reaction Flask

Condenser

Dry Ice and Acetone Traps

Vacuum Pump

Constant Temperature
Bath

Manometer

Vacuum Apparatus
FIG. 1
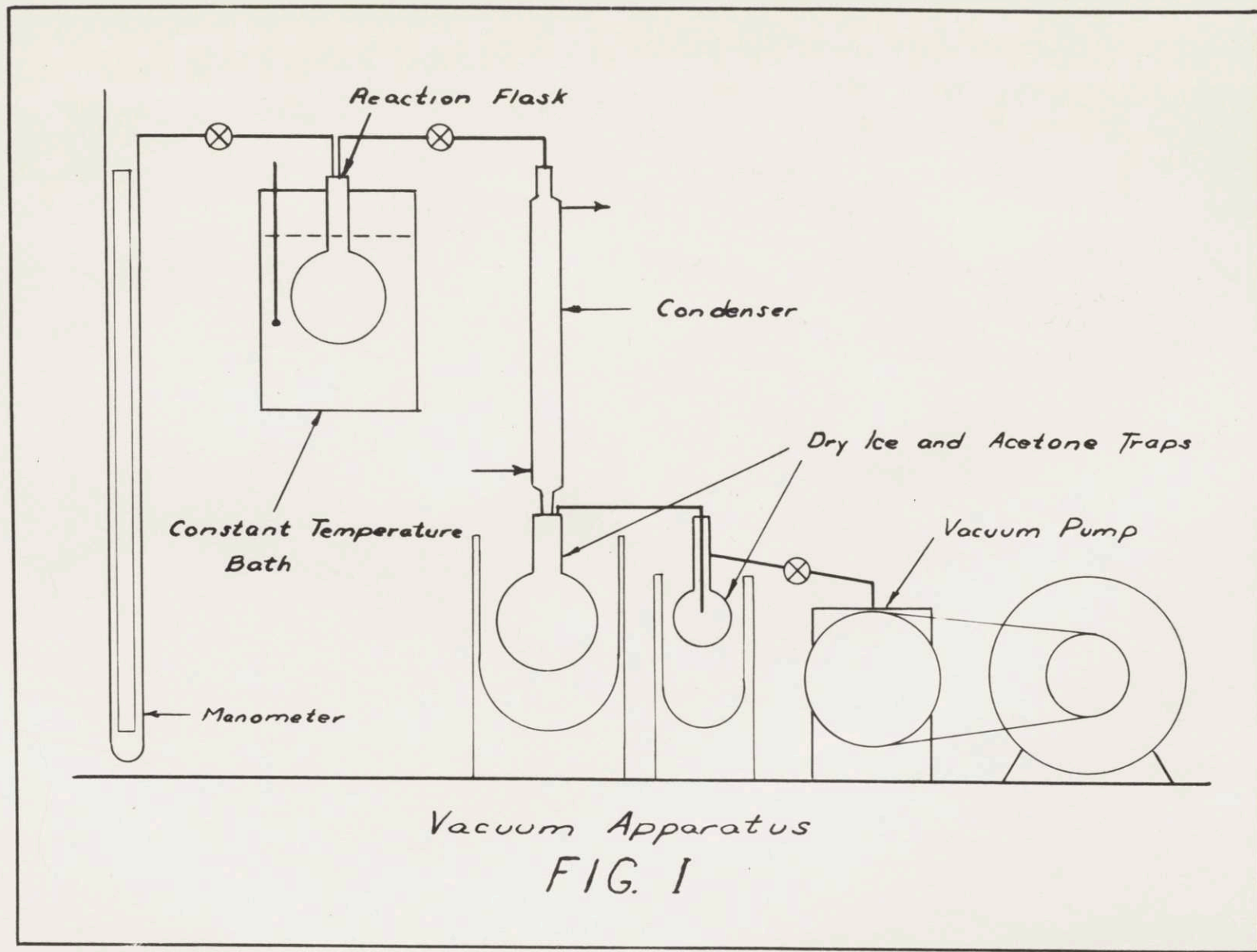
## Procedure II

After quite some experimentation, the following method
of growing the decahydrate crystals around the bulb of a
thermometer was adopted.

A saturated solution of sodium sulfate was boiled,
filtered, and cooled to 25 C.  A small seed crystal was then
introduced into the solution whereupon many needle-like
crystals quickly grew.  After several hours of growth, a
strong, well-formed "needle" was picked and fastened to the
bulb of the thermometer by means of a rubber band.  The bulb
and the crystal were then suspended in a saturated solution,
made as the previously mentioned one, but cooled only to 30 C.
This solution was constantly rotated about the crystal.  With-
in several hours a crystal which covered most of the bulb had
grown.

The wet crystal on the bulb was put in the 600 cc. reaction
flask so as not to touch the walls.  This was done by putting
the thermometer through the rubber stopper and suspending it
down into the flask.  The flask was then slowly evacuated.
(The apparatus used was the same as in Procedure I.)  The man-
ometer and thermometer readings were recorded at the time when
white specks first appeared on the crystal.

## Procedure III

Crystals of $Na_2SO_4 \cdot 10H_2O$ (Reagent) were ground in a ball mill until the size of the particles was less than 1 mm. in diameter. These were then made into a fluidized bed by passing air at about 2 cu. ft./min. (measured by pressure drop across an orifice) through them. (Figure 2) Before entering the bed, the air was humidified by bubbling it through water, the temperature of which was fixed by a constant temperature water jacket. The partial pressure of water vapor entering and leaving the fluidized bed was measured by means of wet and dry bulb thermometer readings. ( Figure 5 ) The fluidized bed jacket temperature was kept constant within 3 C. by a continuous flow of water that was heated by a Bunsen burner before entering the jacket. The temperature of the bed was measured by a thermometer suspended in the center of the reaction zone. By reading and recording the various temperatures at 5 min. intervals, the dehydration of the bed was followed.
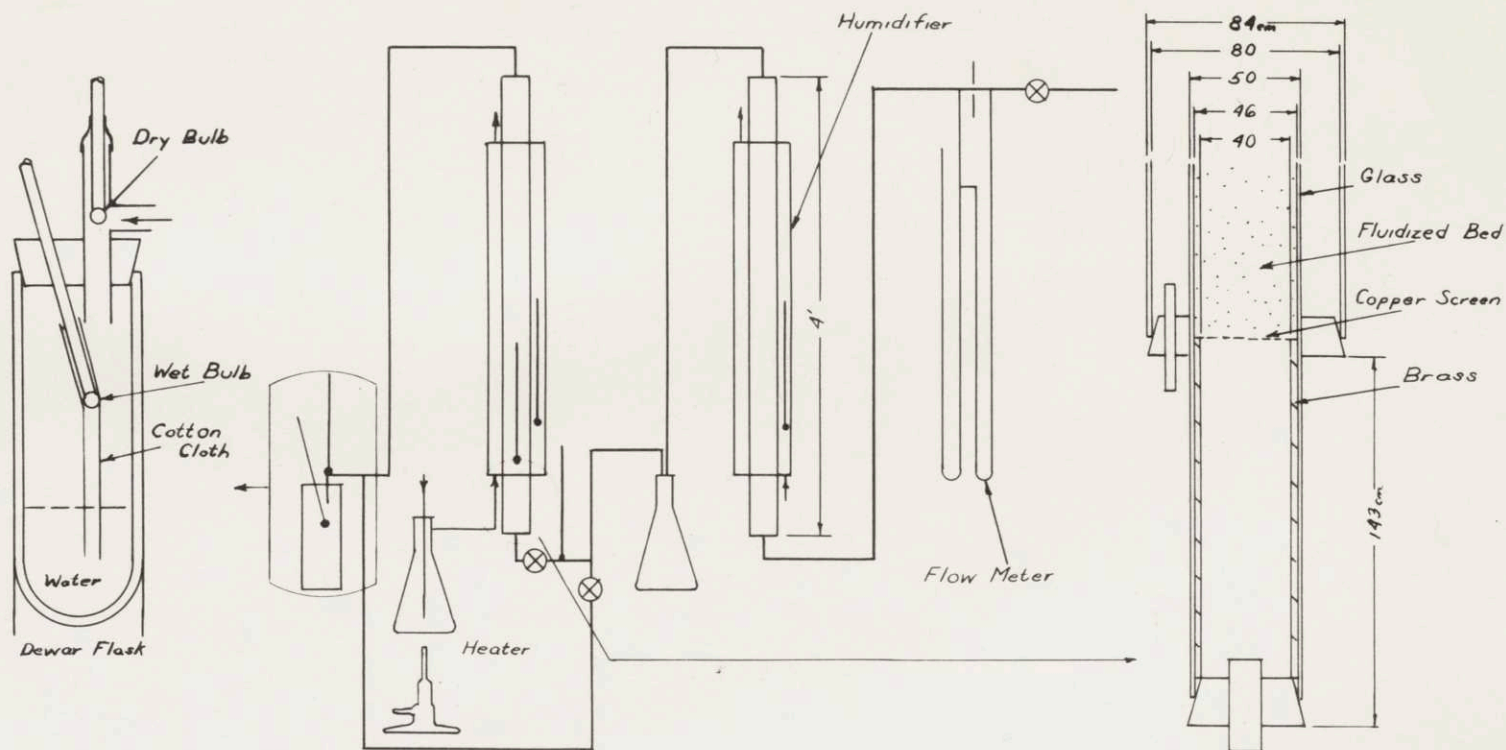
FIG. 2

Fluidized Bed Apparatus

# Results

## Procedure I

It was noted as the pressure was slowly reduced, the first visible change in the reaction flask was the formation of clear needle-like crystals of decahydrate on the wetted sides of the reaction flask. After this solution disappeared, and at about 1.5 mm. (Hg) below the equilibrium pressure of $Na_2SO_4.10H_2O$ corresponding to the bath temperature, white specks appeared on the side crystals. These specks rapidly increased both in number and size. Within several minutes the large crystal bumped as vapor from the solution under it forced its way out. When the pressure reached about 3 to 6 mm. (Hg) below the equilibrium pressure previously mentioned, white specks began to appear on the surface of the large crystal. Figure 3 shows graphically the results of a typical run using Procedure I.

Fig. 3

Dehydration of $Na_2SO_4 \cdot 10H_2O$ Crystal

Run 4 at 29°C, Barometric Pressure 771.9 mm.

Appearance of white on walls

Bumping of large crystals

Appearance of white on large crystal

dissociation pressure

Absolute Pressure in cm. of Hg

Time in minutes

# Results

## Procedure II

As the pressure in the reaction flask was reduced and
neared the equilibrium pressure of the decahydrate, the tem-
perature of the crystal around the thermometer bulb dropped
several degrees. The following table shows the temperature
and pressure at which white spots appeared on the crystals.

|  | Run 1 | Run 2 | Run 3 | Run 4 |
|---|---|---|---|---|
| Barometric Pressure | 769.3 mm | 769.0 | 770.3 | 769.9 |
| Manometer Reading | 754.5 mm | 753.7 | 755.0 | 754.5 |
| Absolute Pressure in Flask | 14.8 mm | 15.3 | 15.3 | 15.4 |
| Crystal Temperature | 21.1 C. | 23.4 | 23.0 | 23.1 |
| Equilibrium Pressure | 14.1 mm | 16.4 | 15.9 | 16.0 |
| $\frac{\text{Equil. Press. - Absol. Press.}}{\text{Equilibrium Press.}}$ | -.049 | .067 | .037 | .037 |

# Results

Procedure III

The results of this procedure are shown graphically in Figure 4. The vapor pressures shown correspond to wet and dry bulb readings. (Figure 5) (Appendix C) Initially the deca- hydrate particles appeared crystaline - glossy and with sharp edges. As time passed and the dehydration reaction proceeded the particles loss their luster and edges off in fine pieces. At the end of the run, the particles were found to be soft on the outside - as the anhydrous sulfate - and hard on the inside - as the decahydrate. The run decomposed about 3/5 of the decahydrate bed.
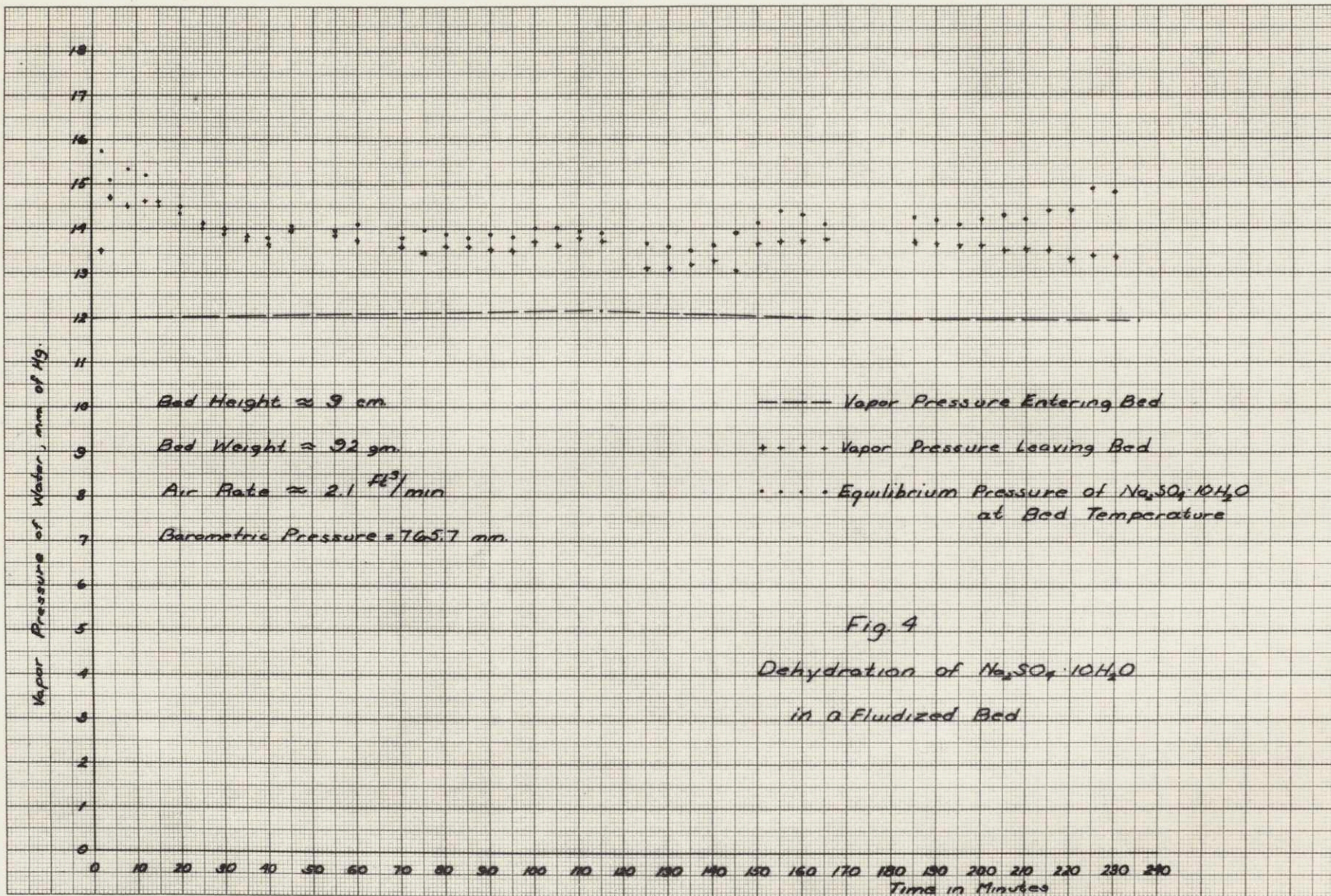
Fig. 4

Dehydration of $Na_2SO_4 \cdot 10H_2O$

in a Fluidized Bed

Bed Height ≈ 9 cm.

Bed Weight ≈ 92 gm.

Air Rate ≈ 2.1 $\frac{ft^3}{min}$

Barometric Pressure = 765.7 mm.

— — — Vapor Pressure Entering Bed

+ + + . Vapor Pressure Leaving Bed

. . . . Equilibrium Pressure of $Na_2SO_4 \cdot 10H_2O$
at Bed Temperature

Vapor Pressure of Water, mm of Hg.

Time in Minutes

## Discussion

In Procedure I, supersaturation of from 3 to 6 mm. (Hg)
was obtained. However, because of the dehydration of the
crystals on the walls of the reaction flask before the initia-
tion of dehydration on the large crystal, some doubt arose as
to the exact temperature of the large crystal. It is thought
that the evaporation and removal of the water from the flask
cooled the solution and crystals down along the vapor pressure
curve of the
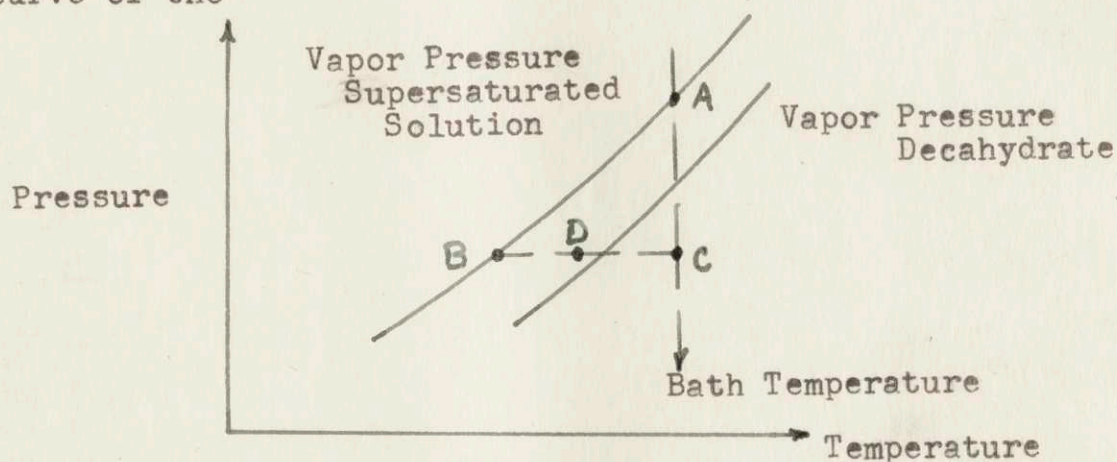


supersaturated solution (A to B). When all the water had been
taken from the flask, the crystals were then heated to the bath
temperature by heat flow from the bath (B to C). The crystals
on the walls heated quickest since they were nearest the source
of heat and also were smaller (thus requiring less heat to
raise their temperature). By the time they reached the bath
temperature they probably were considerable below the vapor
pressure curve of the decahydrate (C) and thus quite super-
saturated. On the other hand, the heat flow to the surface
of the large crystal was not as fast and therefore its tem-
perature was still lower than the bath temperature and above
the vapor pressure curve of the decahydrate (D). This ex-
plains why the crystals on the walls of the flask dehydrated
first.

Notice should be taken of the "peaks" on the curve (Figure 3) at 54 min. and at 74 min. The first one corresponds to the evaporation of the last drops of the solution and the formation of the decahydrate. The second corresponds to the point where the decahydrate begins to turn to the anhydrous sulfate.

To get better temperature reading of the crystals at the point of initial dehydration, it was decided to grow the crystals around the bulb of a thermometer. The idea for this was that the temperature inside the crystal would be the same as on the outside surface where the dehydration process was taking place. This would be true if the heat which was necessary for the reaction flowed from the vapor surrounding the crystal and not through the crystal itself. If there was no heat flow through the crystal, there was no temperature gradient and the temperature inside the crystal was the same as at the reaction zone.

The figures from this procedure (see Results-Procedure II) showed much less supersaturation than the previous procedure. This was due to the better temperature readings. They also are contrary to what Faraday [1] wrote since he supersaturated the crystals enough so that a mere scratch would start the dehydration process.

The reason for this discrepancy was thought to have been that where Faraday's crystals were surrounded by air and water vapor with a total pressure of one atmosphere, my crystals were surrounded by only water vapor. The "partial" pressure of air was thought to have some effect upon the degree of supersaturation obtainable. This was the main reason for carrying out the fluidized bed experiments, since the total pressure would be the sum of the water and air partial pressures.

The results (Figure 4) failed to show any effect of air upon the degree of supersaturation obtained. The vapor pressure of the water in the effluent air was very near to the equilibrium pressure for the decahydrate corresponding to the bed temperature.

As the dehydration of the bed proceeded, the effluent vapor pressure became noticeably lower than the equilibrium pressure, thus indicating that the rate of dehydration was decreasing. Since the results to Procedures I and II show that little supersaturation can be obtained and noticing that a coating of anhydrous sulfate was built up around the decahydrate particles, it is possible that the temperature reading on the bed thermometer.was the temperature of the outside of the particles while the temperature inside at the reaction zone was lower and equal to that corresponding to the effluent vapor pressure. Thus, the coating might have been acting as insulation - blocking the heat flow to the reaction zone.

Another possible explanation for this low vapor pressure might be that the coating formed around the particles prevented the water that was produced by the reaction from diffusing rapidly from the reaction zone.

In view of the facts presented by Lindal and Faraday, the results obtained in this thesis are somewhat startling.

As far as Faraday is concerned, I do not believe he had controlled conditions and thus reliable data.

However, Lindal's data is not to be discarded as unreliable. Since the carbonate superheated and the decahydrate did not, it is reasonable to say that the $CO_2$ is held more strongly to CaO than $H_2O$ to $Na_2SO_4$.

Werner (11) made distinction between first order compounds, such as $H_2O$, NaCl, $SO_3$, etc., which are held together with (Primary) valence forces and compounds of higher order which are formed from combination of first order compounds. When two elements combine to form a compound of the first order, their primary valence forces become saturated. But there is still a field of force around the molecule which enables it to combine with other molecules to form compounds having almost any degree of stability. The molecules are then said to be held by residual or secondary valence forces. According to this theory, both the decahydrate and the carbonate are formed from primary compounds by secondary valence forces. However, the magnitude of these forces must be different for these compounds, since a much higher degree of supersaturation is required for decomposing the carbonate than the decahydrate.

Professor Michaels (6) says that molecular arystals (built up of aggregates of molecules rather than crystals of diamond type, etc.) differ in that some have a big spread between boiling points and melting point, whereas others have little spread or even negative spread. Another way of saying the same thing is that some crystals have very low vapor pressure at their melting point, whereas other have high. The melting point is the point at which thermal agitation of the molecules becomes enough to shake the molecules in the crystals loose and let them slip over into the liquid phase. However, in the liquid phase the molecules are still attracted to each other but the attractions are now different because the arrangement of the molecules is now largely random rather than highly oriented. If the mutual molecular attractions in random arrangements are high relative to those in the oriented arrangements in the crystals, the boiling point of the liquid will be high and the vapor pressure at the melting point low. If the random attractions in the liquid phase are low relative to the oriented attractions in the crystals, the reverse will be the case.

Professor Michaels points out that if the random attractions in the liquid are high, this will interpose an obstacle to rearrangement of the molecules into the crystal orientation, i.e., the tendency of the liquid to supersaturate on cooling below the freezing point will be great. That this correlation exists is indicated by the evidence of such materials as glycol, glycerin, and the higher polyhydric alcohols in which the tendency becomes very great. In other words, if vapor pressure

is high at the melting point, superheating and supersaturation
will tend to be small.  From this point of view, it is very
unfortunate that we picked out sodium sulfate $Na_2SO_4.10H_2O$
to try to get supersaturation.

## Conclusions

The data found in this thesis indicates that abnormally low water vapor pressures - supersaturation - over $Na_2SO_4.10H_2O$ can not be obtained. Also, the factor controlling the dehydration process was found to be either the rate of heat supply to the reaction zone, or the rate of diffusion of water vapor from this zone, or a combination of both.

## Recommendations

(1)  Investigation of $Na_2S_2O_5$ to find if supersaturation can be obtained may put more light on type of reaction studied.

(2)  Investigation of crystal structure of $CaCO_3$ and $Na_2SO_4.10H_2O$ may give some clues as to the difference in the degree of supersaturation obtainable.

APPENDIX

## Appendix A
### Literature Citations

(1) Faraday's statement from (4)

"As a curious illustration of mechanical forces over chemical affinity, I will quote the refusal of certain substances to effloresce when their surfaces are perfect, which yield immediately upon the surface being broken. If crystals of carbonates of soda, or phosphate of soda or sulfate of soda having no part of their surface broken, be preserved from external violence, they will not effloresce. I have thus retained crystals of carbonate of soda perfectly transparent and unchanged from September 1827, to January 1833; and crystals of sulfate of soda from May 1832 to the present time, November 1833. If any part of the surface were broken or scratched, then efflorescences began at that part, and covered the whole. The crystals were merely placed in evaporaring basins and covered with paper."

Since Faraday knew nothing of equilibrium vapor pressures at various temperatures, he took little precaution when scratching these crystals to make sure that the crystals were not at such a state in which they should ordinarily decompose.

(2) Jeremassen, F., and Svanoe, H., - Chem. Met. Eng. Vol. 39 (1939)

(3) La Mer - Ind. Eng. Chem. Vol. 44 (1952) p.1270

(4) Langmuir, I. - Am. Chem. Soc. J. Vol. 38 (1916) p. 2264

(5) Lindal - B.S. Thesis, MIT. 1951

(6) Michaels, Prof. A.S. - Personal Communication

(7) Spencer and Topley - Chem. Soc. Lon. J. (1929) p.2264

(8) Symposium on Nucleation - Ind. Eng. Chem. Vol.44 (1952)

(9) Topley, B. and Hume, W. -Roy. Soc. Lon. Proc. A126
(1928) p.211

(10) Webre, A.L. - Mech. Eng. Vol. 27 (1935)

(11) Werner - from (4)

(12) Zawadski, J. and Bretsnajder, S. - Trans. Far. Soc.
Vol. 34 (1938)

(13) Notes from MIT Course 311, Engineering Metals

# Appendix B

## Fluidized Bed Dehydration of $Na_2SO_4.10H_2O$

Barometric Pressure   765.7 mm.
Air rate   2.1 cu. ft./min.
Bed weight   92 gm.

| Time | Wet Bulb | Dry Bulb | Bed | Bed Jacket | Humid.Jacket | Entering Temp. |
|------|----------|----------|-----|------------|--------------|----------------|
| min. | °C. | °C. | °C. | °C. | °C. | °C. |
| 0 | 16.94 | 21.95 | | 22.9 | 10.5 | 24.3 |
| 2 | 19.0 | 25.0 | 22.7 | 22.75 | 10.5 | 22.8 |
| 4 | 19.7 | 24.8 | 22.1 | | 10.5 | |
| 8 | 19.55 | 24.55 | 22.4 | 22.7 | 10.5 | 22.5 |
| 12 | 19.55 | 24.4 | 22.25 | 23.0 | 10.5 | 22.2 |
| 15 | 19.5 | 24.25 | 21.2 | 22.9 | 10.5 | 22.15 |
| 20 | 19.4 | 24.2 | 21.35 | | 10.4 | |
| 25 | 18.95 | 23.65 | 20.95 | 22.1 | 10.4 | 21.25 |
| 30 | 18.85 | 23.6 | 20.85 | | 10.4 | 21.3 |
| 35 | 18.5 | 23.0 | 20.65 | 21.55 | 10.4 | 20.9 |
| 40 | 18.5 | 23.4 | 20.7 | 21.9 | | |
| 45 | 18.7 | 23.35 | 21.0 | 22.6 | | 20.95 |
| 55 | 18.65 | 23.5 | 20.9 | 22.4 | 10.3 | 20.6 |
| 60 | 18.8 | 23.85 | 21.1 | 23.5 | 10.3 | 20.6 |
| 70 | 18.45 | 23.25 | 20.7 | 21.85 | 10.3 | 20.4 |
| 75 | 18.45 | 23.5 | 20.9 | 22.55 | 10.3 | 20.55 |
| 80 | 18.45 | 23.2 | 20.8 | 22.1 | 10.3 | 20.55 |
| 85 | 18.35 | 23.0 | 20.7 | 21.9 | 10.4 | 20.65 |
| 90 | 18.35 | 22.9 | 20.8 | 22.05 | 10.45 | 20.55 |
| 95 | 18.3 | 23.0 | 20.75 | 22.1 | 10.55 | 20.7 |
| 100 | 18.5 | 23.2 | 21.0 | 22.15 | 10.6 | 20.8 |
| 105 | 18.55 | 23.5 | 21.0 | 21.9 | 10.6 | 20.95 |
| 110 | 18.45 | 22.85 | 20.85 | 22.0 | 10.65 | |
| 115 | 18.4 | 22.8 | 20.9 | | | |
| Check on entering vapor pressure | | | | | | |
| | 16.25 | 19.75 | | | | |
| 125 | 17.9 | 22.5 | 20.6 | 21.0 | 10.6 | 20.35 |
| 130 | 17.8 | 22.3 | 20.45 | 21.15 | 10.5 | |
| 135 | 17.8 | 22.2 | 20.4 | 21.55 | 10.5 | 20.25 |
| 140 | 17.6 | 21.35 | 20.5 | 22.0 | 10.3 | 19.75 |
| 145 | 18.25 | 23.75 | 20.8 | 23.35 | 10.3 | 21.1 |
| 150 | 18.75 | 24.35 | 21.15 | 23.25 | 10.35 | 21.45 |
| 155 | 18.95 | 24.5 | 21.4 | 23.0 | 10.3 | 21.8 |
| 160 | 19.0 | 24.65 | 21.3 | 23.1 | 10.35 | 21.9 |
| 165 | 19.0 | 24.5 | 21.1 | 22.45 | 10.35 | 21.9 |
| Check on entering vapor pressure | | | | | | |
| | 16.6 | 21.0 | | | | |
| 180 | 18.9 | 25.0 | 21.6 | 23.2 | 10.45 | 22.4 |
| 185 | 18.95 | 24.5 | 21.25 | 22.7 | 10.4 | 21.8 |
| 190 | 18.8 | 24.25 | 21.2 | 22.8 | 10.4 | 21.85 |
| 195 | 18.75 | 24.25 | 21.1 | 22.5 | 10.4 | 21.85 |
| 200 | 18.75 | 24.25 | 21.2 | 23.1 | 10.3 | 21.8 |
| 205 | 18.7 | 24.2 | 21.3 | 23.15 | 10.3 | 21.8 |
| 210 | 18.7 | 24.2 | 21.2 | 22.85 | 10.3 | 21.8 |
| 215 | 18.7 | 24.2 | 21.4 | 23.5 | | |
| 225 | 18.8 | 25.0 | 21.4 | 23.3 | 10.5 | 21.65 |
| 235 | 19.2 | 25.9 | 21.8 | 24.35 | 10.45 | 21.65 |
| Check on entering vapor pressure | | | | | | |
| | 16.4 | 20.7 | | | | |

## Appendix C

### Notes on Calculation on Vapor Pressure of Water in Air

The apparatus used to find the vapor pressure of water
in an air stream is shown in Figure 2. It consisted of a
Duwar flask with water in the bottom, a wet bulb covered with
cotton cloth that extended down into the water, and a stream
of air with the vapor passing over the wet bulb. The air
stream velocity in the 12 mm. tubing (just before passing
over the wet bulb) was approximately 29 ft./sec. The dry
bulb was in this same tubing, upstream from the wet bulb. Both
wet and dry bulb thermometers could be read to $0.1^{\circ}C$. From
dry bulb reading, the difference between the wet and dry
readings, and Figure 5, the vapor pressure was found.

Fig. 5

Vapor Pressure of Water in Air
from Wet and Dry Bulb Readings
(from Landoft Bornstein)
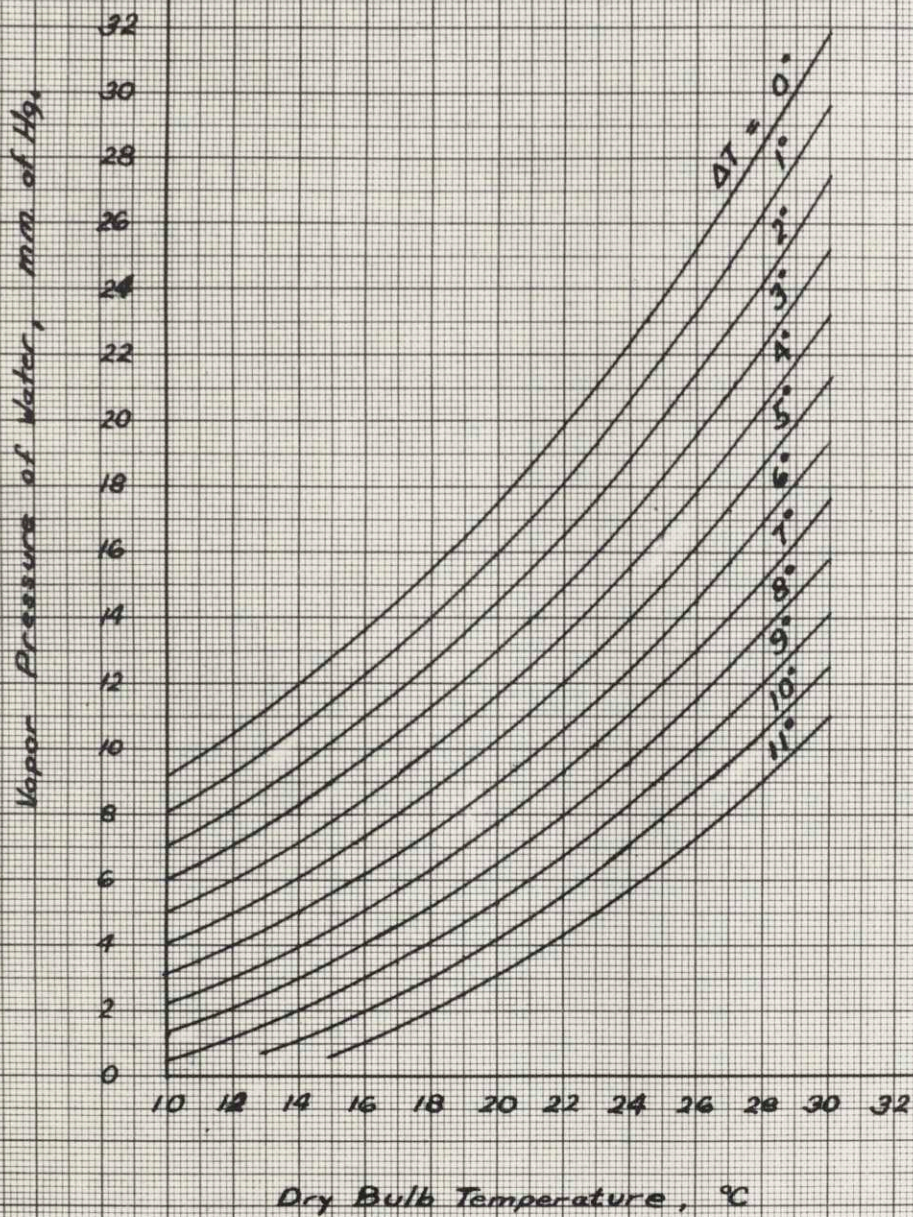
$\Delta T = T°C_{dry\ bulb} - T°C_{wet\ bulb}$

Fig. 6

Solubility of $Na_2SO_4$ in $H_2O$
(Int. Crit. Tables, Vol 4, Pg 236)

$Na_2SO_4$

$Na_2SO_4 \cdot 10 H_2O$

Temperature °C.

Gram mols / 1000 gm. $H_2O$

Fig 7

Calibration Curve for Orifice

Fig. 8

① Vapor Pressure for Water
   from Int. Crit. Tables Vol. 3 Pg 212

② Dissociation Pressure for $Na_2SO_4 \cdot 10H_2O$
   from Int. Crit. Tables Vol. 7 Pg 304

Curve ①

Curve ②

Absolute Pressure, mm of $Hg$

Temperature °C

31.