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RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

PURIFICATION OF CARBON DIOXIDE FOR REACTOR PURPOSES

PART III – DRYING

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ABSTRACT

Comparison of the adsorption characteristics of the desiccants silica gel, alumina, and molecular sieves has shown that molecular sieves have by far the greatest capacity of the desiccants at the low partial pressures considered. Equilibrium data in the form of isotherms were established over the range of variables expected in the coolant circuit of a proposed Australian H.T.G.C. reactor.

The mass transfer from the gas phase to molecular sieves is such that no correlation could be attempted for the adsorption zone height; the height proved to be too small.

CONTENTS

1. INTRODUCTION

In the literature review and recommended programme for work on carbon dioxide purification in the Australian H.T.G.C.R. project (Draycott and Kerr, 1960), it was pointed out that water is the impurity likely to cause most concern. Most of the initial effort in this study has therefore been aimed at elucidation of the variables affecting moisture removal. The three desiccants, silica gel, alumina, and Linde molecular sieves Type 4A were studied individually, although it is likely that a composite bed would be used in the reactor system because of cost considerations. Although Type 4A sieves were studied it is obvious that for applications to carbon dioxide and the impurities water vapour, oxygen, and nitrogen, Type 5A will behave in a similar manner. (Breck et al. 1956).

This report deals with the complete study of these three desiccants and presents results showing the effect and performance of such variables as temperature, pressure, gas velocity, and bed depth.

2. THEORETICAL CONSIDERATIONS

Prediction of the characteristics of the adsorption wave is the most important problem facing designers of fixed bed adsorption equipment. Generally, mathematical predictions are made difficult by the unsteady state of fixed bed adsorption together with the many factors which influence adsorption in such cases.

Rosen (1952) treated fixed bed mass transfer by making certain reasonable simplifications in which he ignored longitudinal diffusion and neglected the kinetics of adsorption. Nevertheless the resulting equations are still difficult to solve and so far no application of this analysis appears to have been made to results obtained from experiments on vapour adsorption.

Hougen and Marshall (1947) simplified the correlations with respect to boundary layer by assuming that the mass transfer across this layer is the controlling factor and that the effect of diffusion of gases into the solid is negligible. The correlation developed by these workers which introduces the concept of the transfer unit is:

$$H_{tog} = \frac{1.42}{A} \left(\frac{d_p G}{\mu} \right)^{0.51} \qquad (1)$$

This correlation was developed from previously published data of experiments on the adsorption of water vapour from air by thin beds of silica gel. Solution of this equation is of far more practical significance than attempts at solution of the more complicated Rosen's relationships.

A further simplified approach was made by Michaels (1952). Although this work concerned kinetic data in fixed bed ion exchange it is directly applicable here. This worker introduced the concept of the adsorption zone; in this zone all conditions are assumed to be essentially unchanged over the period of bed adsorption, except during the initial period of operation of the bed when the region is established.

The exchange zone in this bed is defined as that region within which (at steady state) the solute concentration in the gas flowing through the bed falls from 95 to 5 per cent. of its value in the influent. This choice of limits is purely arbitrary.

Plotting the concentration of solute in the effluent as a function of the total volume collected, characteristic S-curves are obtained of the type shown in Figure 1. When the effluent solute concentration reaches 5 per cent. of its value in the influent, the exchange zone has reached the bottom of the bed. With continuing operation the concentration of the solute in the effluent rises until it reaches 95 per cent. of the value in the influent. At this point the bed is essentially exhausted.

For gas adsorption an equation can be developed for the height of the transfer zone as follows:

$$Z_A = Z \frac{\theta_A}{\theta_E - (1-f)\,\theta_A} \qquad (2)$$

The notation is given in Section 8 and the derivation in the Appendix.

The height of the adsorption zone can therefore be easily calculated from the appropriate S curve in conjunction with the above relationship.

The bed capacity can then be determined from the calculated figures for the adsorption zone. If a bed is operated to the break-through point the only portion of the bed not completely exhausted will be the length at the bottom of the bed corresponding to the adsorption zone. This zone is partially saturated. However, the degree of saturation of the whole bed at break-through is given by

$$S = \frac{Z - (1-f)\, Z_A}{Z} \quad . \qquad (3)$$

For economic design S should approach unity.

The height of the adsorption zone is a measure of the rate of adsorption under a fixed concentration driving force. Factors which affect this height must therefore be those factors affecting the resistance to mass transfer. These are:

- adsorbent material
- adsorbent particle size
- fluid velocity
- fluid properties
- adsorbate concentration in inlet fluid
- adsorbate concentration in adsorbent after reactivation
- temperature
- pressure
- past history of the system

The adsorption height is independent of bed height and cross-section. Thus if the zone height is known for a given adsorption process under specified conditions of the above variables, the capacity of a bed of any desired height and cross-section can be calculated for these conditions.

There is a complete lack of data on dehumidification systems for this method of approach so it is not yet clear that the parameters listed above can be correlated by convenient dimensionless formulae. In the ion exchange process of Michaels (1952), zone height and superficial liquid velocity were correlated in the form

$$Z_A = AV^m \qquad (4)$$

where A and m are constants,

and V is superficial velocity.

It is therefore the aim of this work that similar types of correlations be obtained for drying of carbon dioxide in selected desiccants.

3. EXPERIMENTAL METHOD

All the experiments were carried out on the equipment shown schematically in Figure 2. The carbon dioxide used was supplied from a 6-ton storage tank and was of high commercial purity, the water content usually being lower than 20 p.p.m. Thus in all this work it was necessary to introduce water into the carbon dioxide streams before the drying characteristics of a specific desiccant bed could be determined. This was achieved by saturating a small proportion of the carbon dioxide stream by passing it through a water saturated bed. This vessel was packed with glass beads before being filled with water. Carbon dioxide was introduced at the bottom of the vessel and after percolating through the beads

left through an outlet at the top. The saturation level was kept constant by immersion in a thermostatically controlled water bath. The rate of flow through this unit was very low so that the possibility of particulate water being entrained in the flow of gas was negligible. This by–pass saturation circuit was made to operate at a slightly higher pressure than the adsorption circuit so that the addition of the saturated stream could be controlled by a fine needle valve.

Two types of adsorption beds were used in this work. They were:

(a) a stainless steel vessel – 1¼ inch internal diameter. This vessel was used for the high pressure experiments and was capable of withstanding 150 p.s.i.g.

(b) a copper vessel – ⅞ inch internal diameter which was used for all the low–pressure work and investigations into the effect of temperature.

In all the adsorption experiments carried out above room temperature the carbon dioxide was preheated electrically in the top zone of the insulated adsorption column just prior to passing through the desiccant bed. Thermocouples were used to measure the gas temperatures at the inlet and outlet of the bed while the flow rate was measured by a rotameter situated on the low pressure side of the flow control valve. Sampling points were situated at the inlet and outlet of the bed, which was also fitted with a by–pass. This enabled the moisture level of the gas to be brought up to the requisite level and kept constant prior to tests on the bed itself.

In the initial experiments the performances of the three desiccants, whose physical properties are given in Table 1, were compared under identical bed conditions of temperature, pressure, and gas flow rate. The equilibrium state was never reached in these series. The Karl Fischer method of moisture determination was used to measure inlet and outlet moisture concentrations. However, the moisture contents of the outlet gases from the alumina and molecular sieve beds particularly, were too low to be measured accurately by this method. Later a moisture monitor made by Consolidated Electrodynamics and using the electrolysis principle became available and was used for all subsequent measurements. This instrument is capable of measuring moisture contents down to 0.2 p.p.m. with an accuracy of ± 5 per cent.

Detailed dehumidification experiments were carried out on molecular sieves only, because of their greatly superior characteristics as shown in the early tests. Two separate lines of approach were used. First, in experiments to obtain equilibrium data small beds of molecular sieves (10 grams in the copper vessel) were completely saturated at a series of temperatures and pressures. Temperatures varied from 22 to 90°C and pressures from 5 to 150 p.s.i.g. Complete saturation was considered to exist when the moisture concentrations of both inlet and outlet streams were at the same level. This is sometimes referred to as the exhaustion point. In these experiments the inlet concentration varied from 50 to 400 p.p.m. The flow rate was constant in all this work. At the end of each experiment the change in weight of the bed under consideration was determined. The value was cross–checked with graphs obtained from the moisture concentration and flow rates which were recorded throughout the test. Although this series of experiments gave much of the required information, and since the system under consideration is dynamic, equilibrium data do not satisfy all requirements for complete evaluation of the system. It can be appreciated that frequently two or more adsorbents may have similar equilibrium data, but the kinetics of adsorption may reduce the feasibility of some of the adsorbents for commercial use.

Thus in the second approach a more complete set of dynamic experiments, similar to those carried out on the three desiccants initially, were done on molecular sieves alone. Carbon dioxide containing either 200 or 400 p.p.m. of moisture was passed through beds of molecular sieves (80 g) in the stainless steel vessel at flow rates varying to 0.5 to 1.5 ft/sec. (superficial velocity). All the beds in this work were kept at room temperature. The outlet moisture concentration was measured continually until the break–through point was reached. The point was arbitrarily selected as occurring when the moisture concentration in the outlet stream reached a level of 10 p.p.m.

4. RESULTS

4.1 Comparison of Desiccants

The results obtained from the experiments done to compare performances of the three desiccants; molecular sieves, alumina, and silica gel, are reproduced in Table 2. In each case the silica gel used in these tests was regenerated at 150 °C and alumina (–5+6 mesh B.S.S.) was regenerated at 300 °C before testing. Dry air was used as the purge gas in both cases. The molecular sieves were used in all cases in the "as–received" state. In these conditions the material contained approximately 2.5 per cent. residual moisture.

Experiments were carried out at two pressures, 150 and 20 p.s.i.g. with an inlet moisture concentration of approximately 200 p.p.m. The superficial velocity of the gas was low in all cases.

The outlet moisture concentration in the gas from both the alumina and molecular sieve beds in no case exceeded 5 p.p.m. in the time before break–through occurred. In this respect the performance of these two desiccants was superior to that of silica gel from which outlet moisture levels in the range 10 – 20 p.p.m. were obtained. The velocity and pressure effects seemed small and possibly completely negligible in most cases. The only trend which could be discerned was that at the lowest velocity of 0.16 ft/sec. The outlet moisture concentration from the silica gel bed was lower than the outlet levels obtained with higher velocities. Capacities of all three desiccants were unaffected by either pressure or velocity. The capacity at room temperature of the silica gel bed was constant at 4.2 per cent. that of the alumina at 5.0 to 5.2 per cent. and that of the molecular sieves at 18.0 to 18.7 per cent. These tests clearly showed the superior dehumidification properties of molecular sieves so this desiccant was used in all the detailed experiments reported below.

4.2 Equilibrium Experiments

The aim of the second series of experiments was to obtain equilibrium data for the drying of carbon dioxide by molecular sieves. In this case bed equilibrium capacity was the major factor determined. The effect of variables on outlet moisture level was measured in the third series of experiments. Results were obtained at temperatures of 22 °C (room temperature), 35 °C, 52 °C, 72 °C, and 90 °C at pressures of 5, 50, and 150 p.s.i.g. Detailed results are presented in Table 3 and are also shown in the form of modified isotherms in Figure 3. The effect of temperature on bed capacity is clearly shown in Figure 4. Inlet moisture contents in the range 50 to 400 p.p.m. were used in these tests. It is considered that this would be the normal range of moisture levels to be encountered in the reactor, although at certain periods such as a start–up, higher levels may persist for a short period of time. Much higher levels would obviously exist on the failure of a steam pipe in the heat exchanger. However, this would be classed as a major reactor hazard and would involve a reactor shutdown. Lengthy drying of the coolant would then be required before the reactor could again become operational at temperature.

At each temperature the bed capacity was more or less independent of inlet moisture concentrations over the range studied although in some isotherms a little fall–off in capacity was noted at inlet levels below 100 p.p.m. at the higher temperatures and below 200 p.p.m. at room temperature. The isotherms shown in Figure 3 are therefore fairly flat whereas isotherms for silica gel and alumina fall rapidly to a capacity of 3 – 5 per cent. water adsorbed at much higher partial pressure of water vapour than considered in this work (Draycott and Kerr 1961). The experiments at the higher pressures, that is at a higher partial pressure of water vapour, confirm the flat nature of the isotherms, clearly indicating the value of molecular sieves at low values of partial pressure.

At constant temperature and inlet moisture concentration, pressure had no effect on bed capacity. On the other hand at constant pressure the effect of temperature was appreciable as clearly demonstrated in Figure 4. The capacity of 18.6 per cent. obtained at 22 °C with an inlet concentration of 400 p.p.m. decreased to 10.0 per cent. when the bed was operated at 92 °C. The most rapid decrease occurred between 22 and 50 °C. The decrease in capacity as the temperature increased was the result of an increase in equilibrium partial pressure of water vapour over the molecular sieve desiccant at the higher temperatures. For higher bed capacity, operation at the lowest temperature possible is desirable. This must be compromised with the amount of heat that has to be rejected to operate at low temperatures.

4.3 Dynamic Experiments

In the third phase of the investigation dynamic experiments were used to elucidate the effect of temperature and velocity on outlet concentration and on the adsorption zone height referred to in Section 2. All experiments were done at pressures of 5 p.s.i.g. Results are given in Table 4 in which outlet concentrations are quoted to the nearest 0.5 p.p.m. At any particular temperature superficial velocity had no effect on the outlet moisture concentration provided that the length of the bed was greater than the zone height.

At room temperature, outlet levels were always less than 2 p.p.m. Increasing the temperature to 52°C increased the equilibrium moisture in the outlet to values between 6.5 and 7.5 p.p.m. Outlet concentrations obtained were 18 p.p.m. at 72°C and 27 p.p.m. at 90°C. The whole series of results is also shown in Figure 5. From this graph the minimum obtainable dew point at any temperature can be readily obtained. Some figures quoted by Linde (1958) for molecular sieves with different residual moisture contents are also included on this graph. These figures were for the drying of air. The slight variation in slope and relative position may be due to the attraction of molecular sieves for carbon dioxide.

The height of the adsorption zone, Z_A, was calculated from the initial bed depth and measured times to reach break-through and exhaustion points from Equation 2.

In the first instance f was calculated from the S curve and found to be approximately 0.5. In all other instances f was taken to be 0.5. The height of the adsorption zone was constant over the range of variables studied and was between 2 and 3 inches. This value is so small that it can be completely neglected in most design studies.

5. REGENERATION

Regeneration of the molecular sieves after the adsorption cycle is of great importance as it is upon the efficiency of regeneration that the efficiency of the adsorption cycle depends. The normal methods of regeneration using a purge gas of low relative humidity and countercurrent flow are applicable and need no discussion.

The Linde Company (1958) has published data suitable for design purposes on the residual water left in the molecular sieves after regeneration at temperatures up to 650°F (343°C) using a purge gas with a dew point between −40°F and +80°F. The results of the present work have been shown to be consistent with these data, and it was thought unnecessary to carry out detailed work on the regeneration of molecular sieves.

6. DISCUSSION

The results given in the previous section on

1. comparison of desiccants

and 2. the equilibrium data for molecular sieves

need no explanation. It seems clear that molecular sieves will be used as desiccant in the Australian High Temperature Gas Cooled Reactor to obtain economically the required low moisture concentrations. Although the cost of molecular sieves is approximately four times that of alumina, this is offset by a lower capital cost of plant because of the higher capacities achieved.

It was mentioned in Section 4.3, that the aim was to obtain a correlation for the height of the mass transfer zone, a height that would be invaluable in design work. However the rate of mass transfer from the bulk of the gas phase through the boundary layer and into the pores of the molecular sieve is very rapid even when the sieve is nearly saturated. This explains the very small height of the transfer zone. The errors involved in the selection of the break-through point from the adsorption curve are such as not to warrant further accuracy than that quoted in Table 4. It is obvious that no correlation could be obtained. However one point has been made clear. In the adsorption of water by molecular sieves in a fixed bed, the bed may be completely designed on equilibrium figures with the addition of only a few inches in height to allow for the mass transfer zone.

7. CONCLUSION

It can be appreciated that consideration can only be given to alumina and molecular sieves as desiccants suitable for the drying of a reactor coolant. The whole basis of design must be an economic one and this will limit markedly the minimum attainable dew point. It will be impracticable to cool the by-pass gas through the purification circuit to such an extent that the dew point is below $-70\,^{\circ}C$ i.e. 3.0 p.p.m. For this condition, too close a temperature approach with the cooling water would be required and the heat losses could become significant.

The results of this study, together with the published data on alumina and a reliable cost index, are sufficient for a detailed drier design study to be made now.

8. NOTATION

a = external area of adsorbent particles, ft^2/ft^3 .

f = fractional ability of adsorbent zone to adsorb solute, dimensionless.

G_S = flow rate of solvent gas, $lb/hr\ ft^2$.

m = constant.

S = degree of saturation, dimensionless.

U = solute adsorbed in the adsorption zone, $lb/hr\ ft^2$.

V = superficial velocity, ft/hr.

W = quantity of solute-free effluent, lb/ft^2 .

W_A = $W_E - W_B$

W_B = quantity of solute-free effluent at break point, lb/ft^2 .

W_E = quantity of solute-free effluent at exhaustion, lb/ft^2.

Y = concentration of solute in fluid, lb solute/lb solvent.

Y_B = concentration of solute in effluent at break point, lb solute/lb solvent.

Y_E = concentration of solute in effluent at exhaustion point, lb solute/lb solvent.

Y_o = initial concentration of solute in fluid, lb solute/lb solvent

Z = height of the adsorber, ft.

Z_A = height of the adsorption zone, ft.

θ_A = time required for adsorption zone to move a distance Z_A through the bed, hr.

θ_E = time required to reach bed exhaustion, hr.

θ_F = time of formation of adsorption zone, hr.

9. REFERENCES

Breck, O.W., Eversole, W.G., Milton, R.M., Reed, T.B., and Thomas, T.L., (1956).- Crystalline zeolites I The properties of a new synthetic zeolite, Type A. J. Am. Chem. Soc. 78: 5963.

Draycott, A., and Kerr, A.C. (1961).- Purification of carbon dioxide for reactor purposes. Part 1. AAEC/E58.

Hougen, O.A., and Marshall, W.R. (1947).- Chem. Eng. Prog. 43: 197.

Linde, (1958).- Dry gas? Bulletin of Union Carbide.

Michaels, A.S., (1952).- Simplified method of interpreting kinetic data in fixed-bed ion exchange. Ind. Eng. Chem. 44: 1922.

Rosen, J.P. (1952).- Kinetics of a fixed bed system for solid diffusion into spherical particles. J. Chem. Phy., 20: 387.

APPENDIX

SOLUTION FOR THE HEIGHT OF THE MASS TRANSFER ZONE IN AN ADSORPTION PROCESS

The following is a development of Michael's (1952) solution for the height of the mass transfer zone in an adsorption process. The characteristic S–curve of the cycle is shown in Figure 1.

Let G_s be the flow rate of the solvent gas per unit area

W the total solute–free effluent per unit area of bed after any time

Y_B break point concentration of solute in solvent

Y_E exhaustion point concentration of solute in solvent

Y_o initial concentration of solute in solvent.

Therefore, effluent accumulated during the period of transition from Y_B to Y_E is W_A

and $$W_A = W_E - W_B$$

The adsorption zone Z_A ft. which is of constant height is defined as being that height of bed in which the concentration changes from Y_B to Y_E at any time.

Thus if θ_A is the time required for this adsorption zone to move its own height down the column

$$\theta_A = \frac{W_A}{G_S}$$

Also θ_E the time required for the adsorption zone to establish itself and move out of the bed is given by

$$\theta_E = \frac{W_E}{G_S}$$

The bed height Z and θ_F the time required for the formation of the zone can be related to Z_A thus

$$Z_A = Z \frac{\theta_A}{\theta_E - \theta_F}$$

The quantity of solute removed from the gas in the adsorption zone from breakthrough point to exhaustion point is defined as U lb. of solute/sq.ft. of bed.

$$\text{Then} \qquad U = \int_{W_B}^{W_E} (Y_o - Y)\, dW$$

If the adsorbent in the adsorption zone were completely saturated it would contain $Y_o W_A$ lb. solute/ft^2. Thus at the breakthrough point, f, the fraction of the total adsorption bed in the zone which still possesses the ability to remove solute is given by

$$F = \frac{U}{Y_o W_A} = \frac{\int_{W_B}^{W_E} (Y_o - Y)\, dW}{Y_o W_A}$$

The limiting conditions for f exist when f = 0 and f = 1.

$$\text{Then} \qquad \theta_F = (1 - f)\, \theta_A$$

So substituting for θ_F in the above expression for Z_A

$$Z_A = Z \frac{\theta_A}{\theta_E - (1 - f)\, \theta_A}$$

$$= Z \frac{W_A}{W_A - (1 - f) W_A}$$

TABLE 1

PHYSICAL PROPERTIES OF THE THREE DESICCANTS

	Silica Gel	Activated Alumina	Molecular Sieves
Bulk density lb/ft²	38–45	49–55	43–45
Apparent density	0.7	1.6	1.55
Specific gravity	2.1 – 2.3	3.25 – 3.35	
Specific heat BTU/lb °F	0.22	0.24	0.25
Thermal conductivity BTU/ft²/hr °F/in	1	1.0 100 °F 1.45 200 °F	3.9
Reactivation temperature °F	300–350	350–600	350–660
Particle shape	granular	granular	cylindrical pellets

TABLE 2

COMPARISON OF PERFORMANCES OF THE THREE DESICCANTS

Pressure p.s.i.g.	Velocity ft/sec.	Silica Gel –6 +8 B.S.S.		Alumina –6 +8 B.S.S.		Molecular Sieves 4A	
		Outlet Moisture Level in CO_2 p.p.m.	Per Cent. Capacity Adsorbed	Outlet Moisture Level in CO_2 p.p.m.	Per Cent. Capacity Adsorbed	Outlet Moisture Level in CO_2 p.p.m.	Per Cent. Capacity Adsorbed
150	0.16	10–20	4.2	< 5	5.2	< 5	18.5
150	0.40	15–20	4.3	< 5	5.0	< 5	18.0
150	0.70	15–20	4.2	< 5	5.0	< 5	18.7
20	0.42	15	4.2	< 5	5.1		

TABLE 3

EQUILIBRIUM DATA OF MOLECULAR SIEVES

Pressure	Temperature °C	Inlet Moisture p.p.m.	Equilibrium Capacity Per Cent. on Dry Bases
5	22	50	16.5
		120	17.6
		200	18.3
		400	18.6
	35	60	14.1
		110	14.8
		225	15.2
		350	15.4
	52	80	11.7
		150	12.2
		300	12.7
		400	12.9
	72	60	10.4
		170	11.2
		250	11.4
		380	11.6
	90	60	9.1
		180	9.6
		300	9.7
		400	10.0
50	22	190	18.1
		400	18.7
	72	180	11.3
	90	390	10.0
150	22	210	18.3
		320	18.4

TABLE 4

RESULTS OF DYNAMIC EXPERIMENTS

Pressure: 5 p.s.i.g.

Inlet Concentration p.p.m.	Temperature °C	Superficial Velocity ft/sec.	Minimum Outlet Concentration p.p.m.	Z_A in.
100	22	0.3	1.5	2
		0.7	1.5	2
		1.0	2.0	3
		1.5	1.5	2
	52	1.0	7.5	2
		0.3	8.0	2
200	22	0.7	2.0	3
		1.0	1.0	2
		1.5	1.5	2
	52	0.5	6.5	3
	72	0.5	18.0	2
	90	0.5	27.0	2
400	22	0.3	1.5	3
		0.5	2.0	2
		1.5	1.5	2

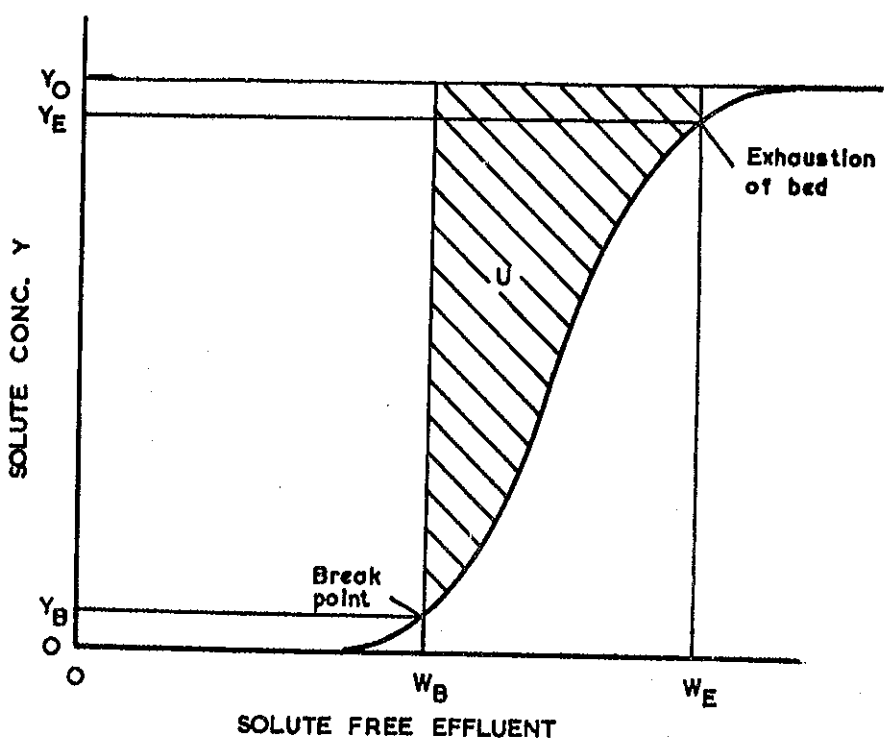

FIG.I. IDEALIZED ADSORPTION CURVE

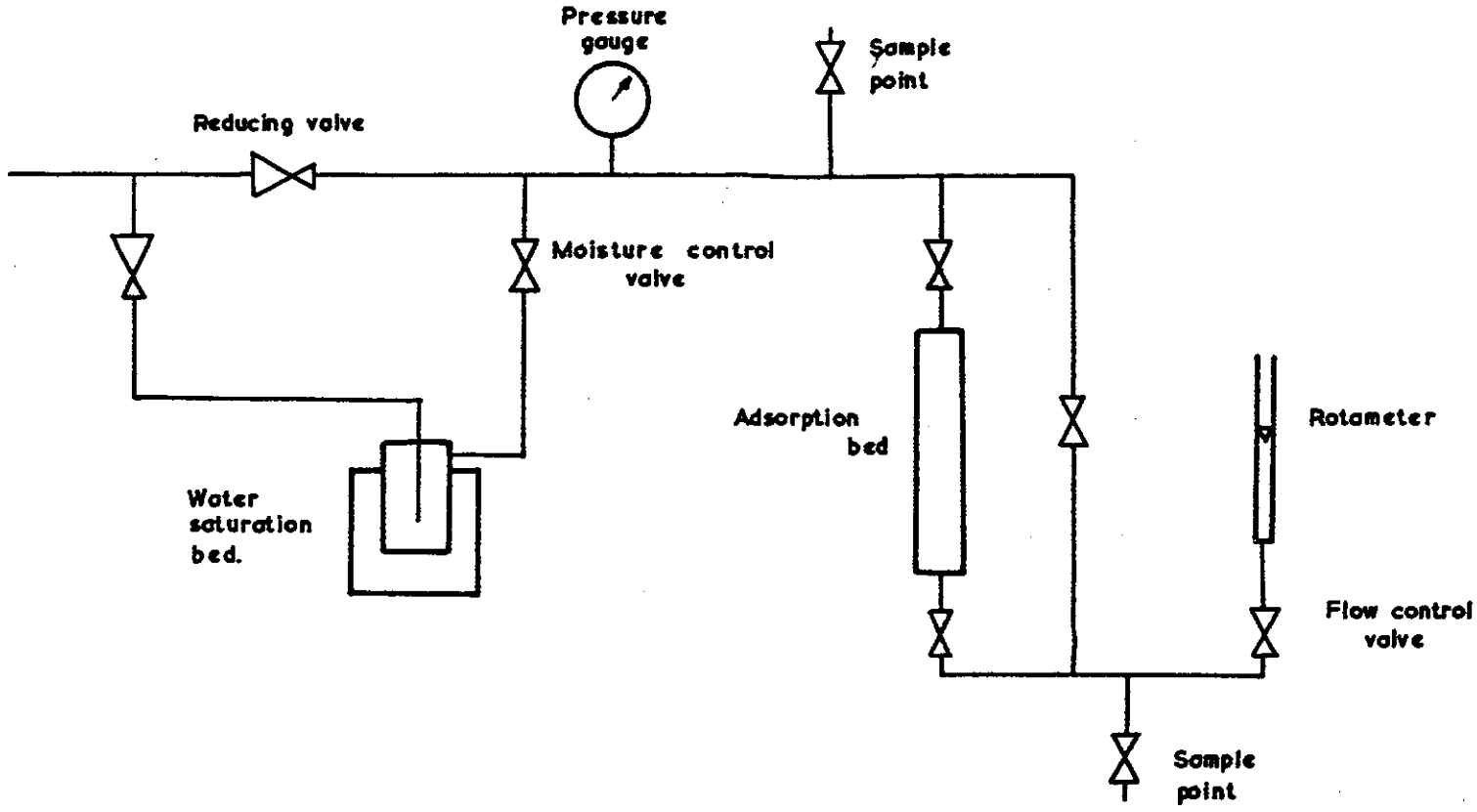

FIG. 2. SCHEMATIC DIAGRAM OF EXPERIMENTAL APPARATUS

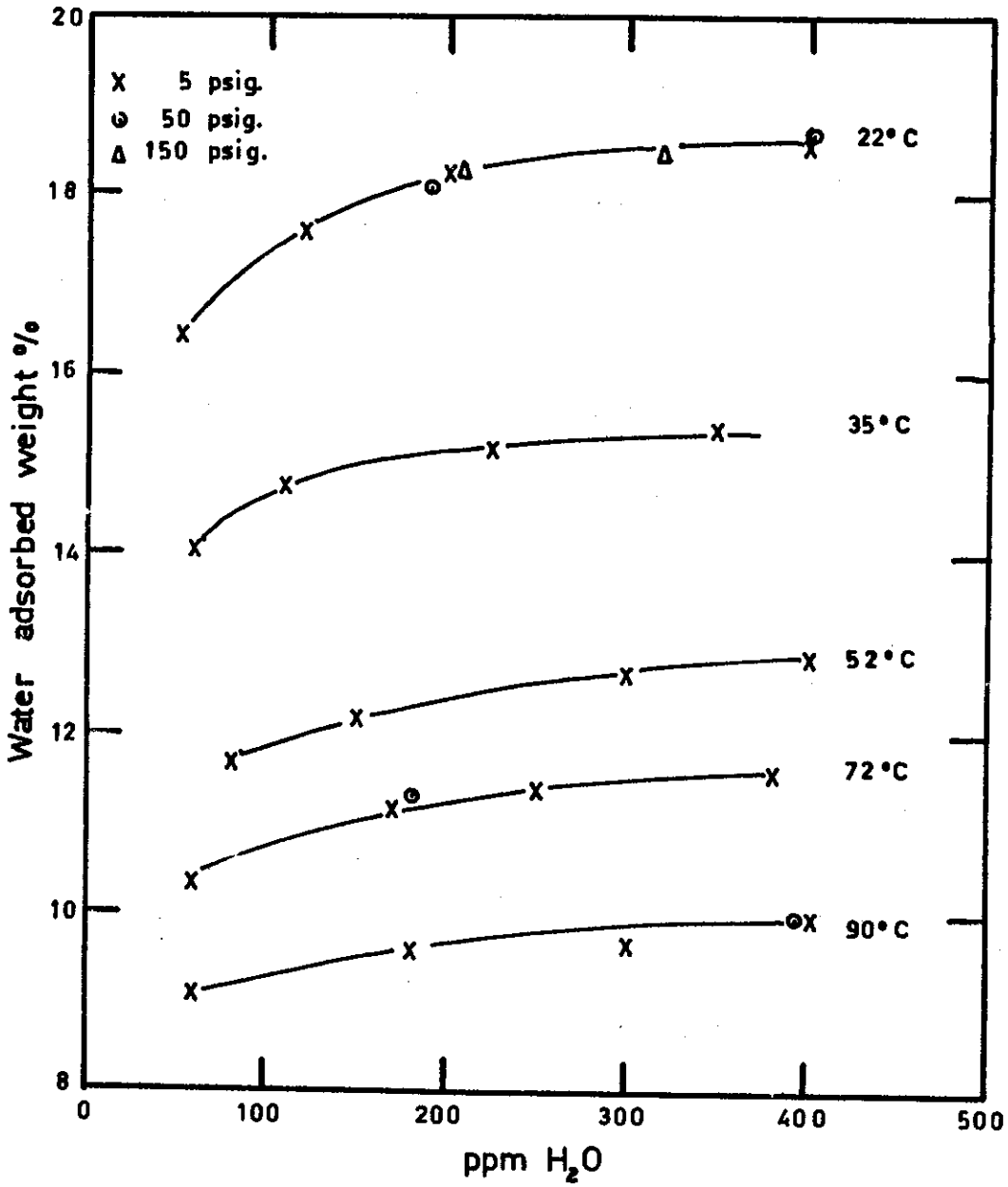

FIG. 3 ISOTHERMS FOR MOLECULAR SIEVES TYPE 4A

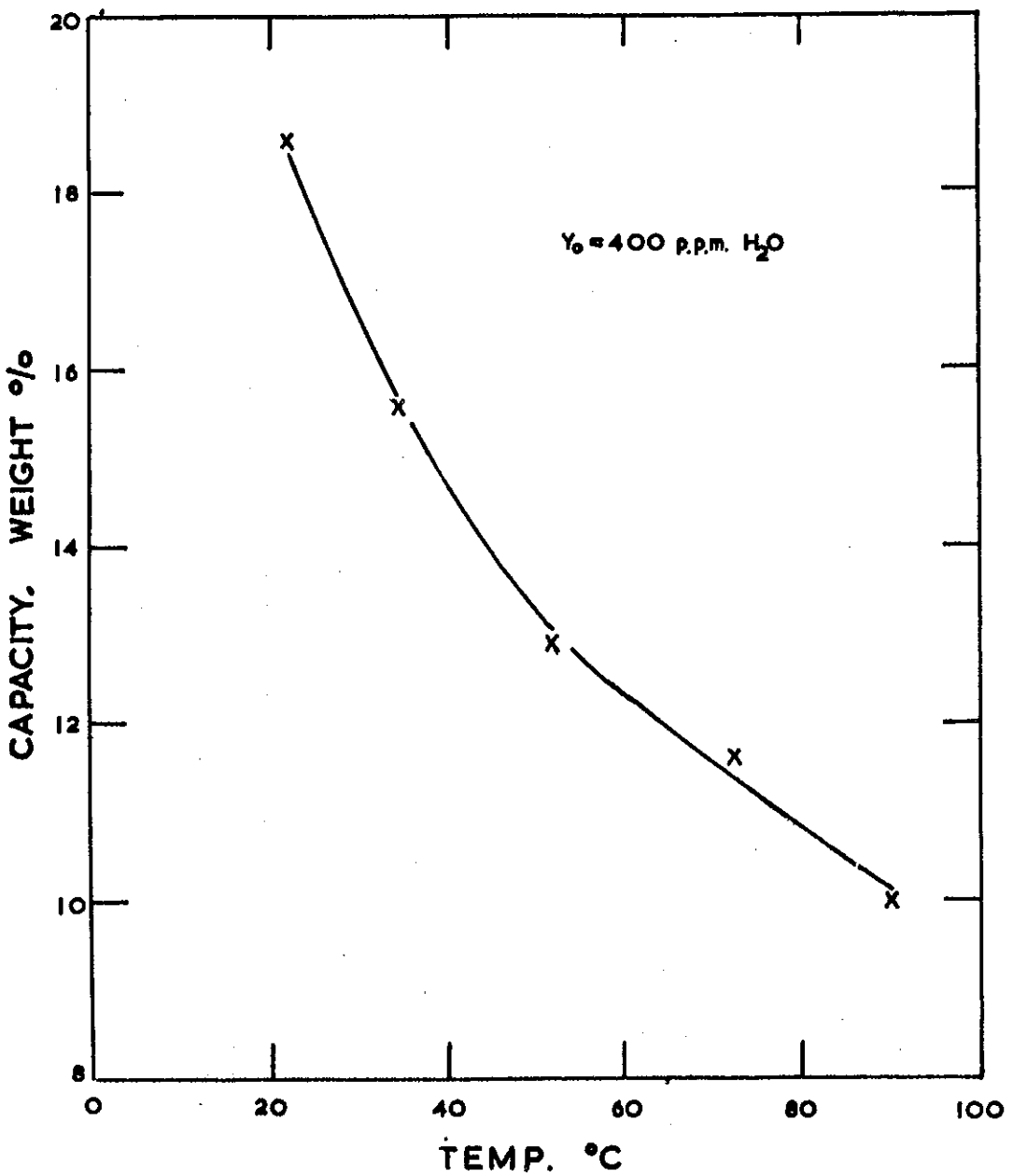

FIG. 4 TEMPERATURE EFFECT ON ADSORPTION CAPACITY

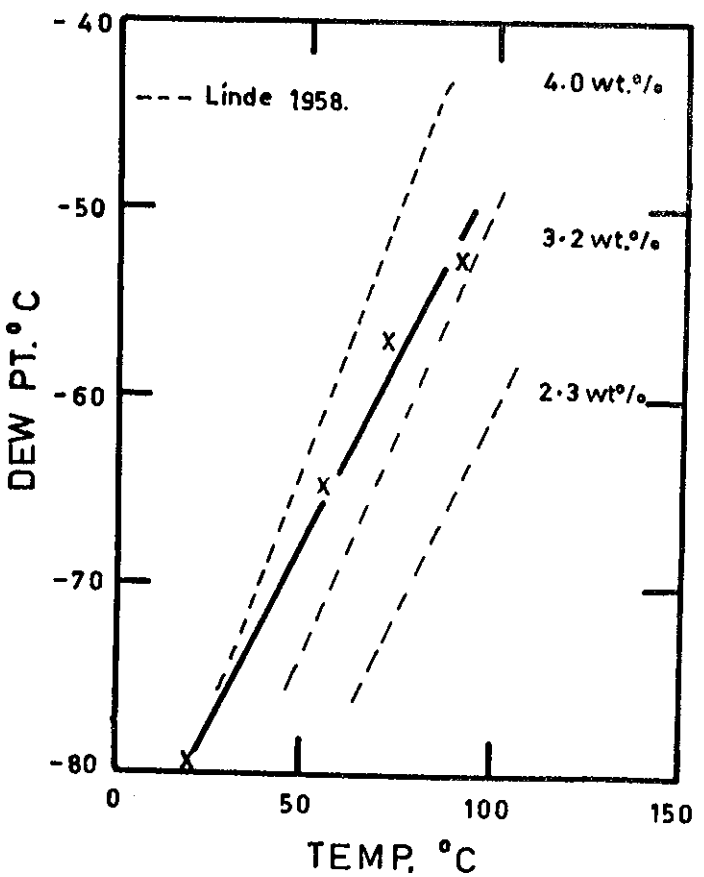

FIG. 5. MINIMUM DEW POINT