Study of Transition Temperatures through Mixed Crystal Formations.   Part-III*.

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It has been previously reported that a new method has been developed in determining transition temperatures with a radioactive isotopes.   The component whose transition temperature is to be determined is at tracer level and does not manifest its existence as such but gives its evidence through mixed crystal formation.   Study of distribution coefficient of a morphologically analogous host having a greater range of stability with the guest at tracer level gives a prominent break at the transition temperatures of the guest component.   This new method of approach has been applied in the present investigation to the study of transition temperatures of orthorhombic and monoclinic $MnSO_4.7H_2O–6H_2O$.   Ferrous sulphate ($FeSO_4.7H_2O$) was taken as host for monoclinic variety and $MgSO_4.7H_2O$ was the host for orthorhombic variety.   Homogeneous distribution factors at different temperatures was studied with these two hosts and ^{54}Mn as guest at tracer level.   Transition temperatures of orthorhombic and monoclinic variety of $MnSO_4.7H_2O–6H_2O$ has been found respectively to be $10° \pm 0·5°$ and $10·5° \pm 0·5°$.   Orthorhombic $MnSO_4.7H_2O$ is metastable with respect to monoclinic variety.   The transition temperatures of these two varieties are near about the same and similar to $ZnSO_4.7H_2O$ which has been previously reported[1,2].

In the previous investigations[1,2] it has been shown that transition temperature of a guest component in a mixed crystal forming system where the host has got a bigger range of stability can be determined by the study of homogeneous distribution factor, (D), with a radioactive isotope of the guest at a tracer level.   Thus the transition temperature of $CoSO_4.7H_2O–6H_2O$ was determined with ^{60}Co as guest and $FeSO_4.7H_2O$ as host.

Vitriols are described as dimorphous.   One form is stable whereas other variety is generally metastable with respect to the stable variety.   Present work refers to the study of transition temperature of the two varieties of the heptahydrated manganous sulphate. $FeSO_4.7H_2O$ (monoclinic) and $MgSO_4.7H_2O$ (orthorhombic) were taken as hosts and ^{54}Mn was taken as the measuring indicator for the guest component.   Distribution study of ^{54}Mn as guest with these hosts at different temperatures were made as described in the experimental section.

EXPERIMENTAL

Experimental precautions and techniques were those like described in the previous communication[1].   Carrier free ^{54}Mn was procured from Bhabha Atomic Research Centre as chloride in dilute hydrochloric acid solution.   A portion of the ^{54}Mn was taken in a beaker

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*. First and second papers of the series have been published under the title : "Application of Radioactive isotopes in the study of transition temperature"[1,2].

1.   B. C. Purkayastha and Samir Sarkar, *J. Inorg. Nucl. Chem.*, 1966, **28**, 347.

2.   B. C. Purkayastha and Samir Sarkar, *J. Indian Chem. Soc.*, 1968, **46**, 787.

and a finite quantity of inactive manganese was added. It was precipitated by adding sodium hydroxide solution. The precipitate containing ^{54}Mn was thoroughly washed. It was finally dissolved in dilute sulphuric acid solution containing a trace of sulphur dioxide. Stock solution containing radioactive isotope thus made were used in the investigations. D was then calculated from the following expression[3].

$$\left(\frac{\text{Tracer}}{\text{Carrier}}\right)_{\text{solid}} \qquad = D \left(\frac{\text{Tracer}}{\text{Carrier}}\right)_{\text{solution}}$$

A few typical data are given in Table 1   Results of the study are shown in figures.

DISCUSSION

Minimum time required for the attainment of equilibrium as is done in this type of investigations[1,2] have been shown Figs. 1 and 2. It will be evident from the figures that equilibrium is attained in two days in both these cases. We have added one more day in the period of equilibration in deriving the values of the distribution factors.
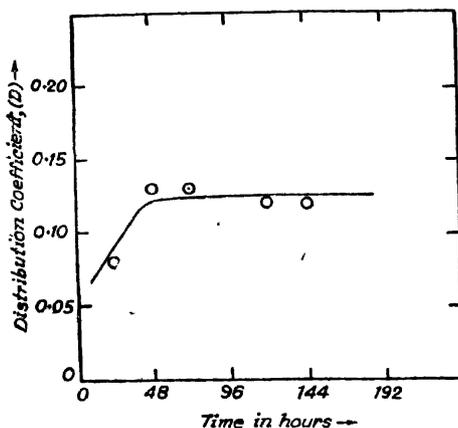

Fig. 1. Distribution of ^{54}Mn between $FeSO_4.7H_2O$ crystals and its saturated solution in $0.5N$ H_2SO_4 at 7° showing the attainment of equilibrium.
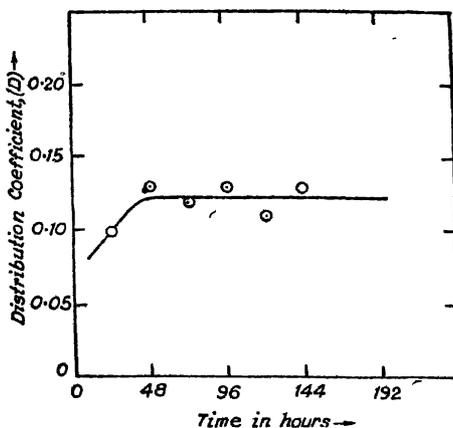
Fig. 2. Distribution of ^{54}Mn between $MgSO_4.7H_2O$ crystals and its saturated solution in $0.5N$ H_2SO_4 at 7°. showing the attainment of equilibrium.

3.   L. M. Henderson and F. C. Kracek, *J. Amer. Chem. Soc.*, 1927, **49**, 738.

TABLE 1

The distribution of ^{54}Mn as guest component between preformed hosts like $FeSO_4$.$7H_2O$ and $MgSO_4.7H_2O$ and their saturated solutions in 0.5 N H_2SO_4.

	Temperature (°C)	Host components	Guest components and initial concentration	Fraction of the host components in the solid phase (%)	Fraction of the tracer in solid phase (%)		D
(a)	5	$FeSO_4.7H_2O$	^{54}Mn (1.0×10^{-3} M)	65.86	13.36		0.080
				55.60	11.15		0.100
				45.86	8.22		0.079
				36.82	4.40		0.079
						Av.	0.091
(b)	20	,, ,,	,, ,,	60.70	16.00		0.124
				50.55	12.04		0.134
				40.70	9.85		0.159
				30.80	6.51		0.156
						Av.	0.156
(c)	7	$MgSO_4.7H_2O$	,, ,,	45.63	10.10		0.134
				37.90	6.31		0.110
				27.14	4.17		0.117
				17.33	6.31		0.321
						Av.	0.170
(d)	22	,, ,,	,, ,,	50.86	12.94		0.144
				38.30	8.03		0.141
				30.90	5.86		0.140
				20.18	4.89		0.203
						Av.	0.157
(e)	3	$FeSO_4.7H_2O$	,, ,,	67.10	16.44		0.096
				69.20	16.75		0.090
				67.30	16.44		0.096
				69.05	15.88		0.085
						Av.	0.092
(f)	20	,, ,,	,, ,,	57.32	15.56		0.141
				58.00	15.56		0.134
				57.16	17.40		0.158
				60.24	15.30		0.119
						Av.	0.138
(g)	5	$MgSO_4.7H_2O$	,, ,,	51.40	11.15		0.119
				51.40	9.70		0.102
				53.67	10.60		0.102
				51.04	8.24		0.086
						Av.	0.102
(h)	22	,, ,,	,, ,,	48.32	9.45		0.112
				48.07	9.89		0.119
				48.20	10.86		0.129
				49.12	10.32		0.119
						Av.	0.119

A glance at Table 1 (a to d) will show that in case of both $FeSO_4.7H_2O$ (monoclinic) and $MgSO_4.7H_2O$ (orthorhombic) as hosts and [54]Mn as guest the distribution factors come out constant. It can, therefore, be inferred that in both the cases hosts take up the guests component through mixed crystal formation. Constancy of homogeneous distribution factor, (D), has also been observed above the transition temperature of the guest component in both the cases.

In view of the fact that statistical error becomes bigger if we take different amount of host components; we equilibrated[1,2], near about the same amount of host components in a saturated solution of the host incorporated with the guest in question. Each point in the figures refer to an average of three or four sets of such computations. A glance at Table 1 (e to h) will show the magnitude of the error involved.
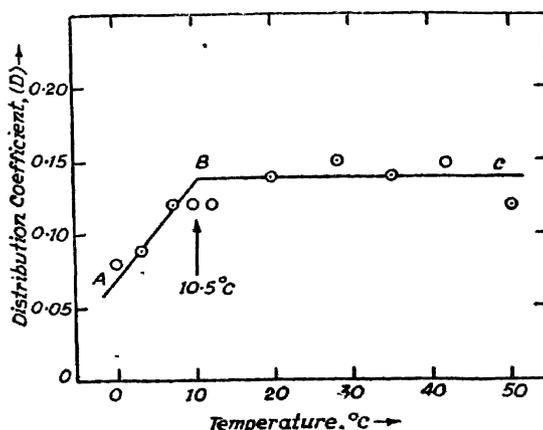

Fig. 3. On the study of the transition temperature of $MnSO_4.7H_2O$ with $FeSO_4.7H_2O$ as host and [54]Mn as guest.

N.B.   Concentration of ferrous iron in the saturated solution at 35° was 2.15M and that of natural manganese was $1.0 \times 10^{-3} M$ in 0.5N H_2SO_4.
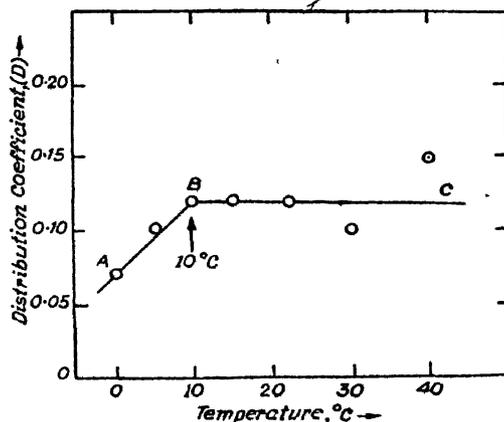

Fig. 4.   Transition temperature of orthorhombic $MnSO_4.7H_2O$ through mixed crystal formation between $MgSO_4.7H_2O$ as host and [54]Mn as guest.

N.B.   Concentration of magnesium in the saturated solution at 35° was 3.15M and that of natural manganese was $1.0 \times 10^{-3} M$ in 0.5N H_2SO_4.

A glance at figure 3 will show that the homogeneous distribution factor (D), in the system $FeSO_4.7H_2O$–[54]Mn rises linearly with temperature and shows a break at about 10.5°, after which temperature the plot becomes parallel to the temperature axis. Change in the partition values is due to the transition of the guest component. Because solubility of $FeSO_4.7H_2O$ describes a straight line and there is no such break at this temperature. It is, however, a known system and transition point as determined by other method is 9.1°. Uptake of [54]Mn by $MgSO_4.7H_2O$ is, however, very interesting (vide fig. 4). Though vitriols are known to be dimorphous yet orthorhombic $MnSO_4.7H_2O$ has never been isolated and as such the question of a transition can never be thought of. But the success of our method is that we have been able to show its existence and the temperature at which the transition to the lower hydrates take place. We have described in our previous communications[1,2] that there is one unstable variety of monoclinic $ZnSO_4.7H_2O$ which has got near about the same transition temperature as that of the orthorhombic variety. By our new method we find that $MnSO_4.7H_2O$ behaves also in a similar way.

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