SHORT PAPER

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Solute–solvent effects on the dissociation of oxalic acid in aqueous mixtures of ethylene glycol solvent at different temperatures†

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The dependence of the dissociation constants of oxalic acid on temperature and composition of ethylene glycol–water binary mixtures have been studied. Thermodynamic and extrathermodynamic analysis of the obtained results have been examined. The p*K* values have been correlated with the dielectric constant of the medium according to Born's electrostatic equation.

Keywords: dissociation contants, oxalic acid, ethylene glycol

The dissociation of weak acids in mixed solvents is known to be a function not only of electrostatic effects but is also largely influenced by specific solvation of the acid and its conjugate base. An empirical approach to clarify the dependence of the dissociation constants of some weak acids on temperature and composition of the solvent was reported.[1,2] This study is consequently a part of systematic research regarding the influence of the solvent on the dissociation constants of weak electrolytes which is a subject of great interest in chemical and biomedical analysis. Accordingly, attempts[3] have been made to correlate the pK^w values in water, with those in different mixed solvent media, pK^s. Also the dependence of acid dissociation constant on the dielectric constant of the medium was discussed.[4,5] Moreover, thermodynamic investigations for acid dissociation reactions in water-organic mixed solvent[6-9] contribute $\Delta H°$ and $\Delta S°$ data to help understand solute-solvent interactions. The present paper reports a study of the first and second dissociation constants of oxalic acid by an EMF method10 in ethylene glycol–water media of varying solvent compositions (0 – 50 wt % ethylene glycol) within the temperature range (30 – 60 °C).

The acid (BDH, Analar) under investigation as recrystallised and dried. Pure co-solvent ethylene glycol (BDH, Analar) was further redistilled and mixtures were prepared using double distilled water. Stock solutions of HCl (= 0.2 mol/kg) were analysed by AgCl weighings , and Na_2CO_3 (dried at 300 °C for 3h) were made up by weight from (BDH., Analar) samples.

An Orion 290 A pH-meter reading to ± 0.1 mV was used , its electrode is a combination low maintenance triode pH electrode with an Ag/Ag Cl internal reference system, sealed reference and built-in thermistor for automatic temperature compensation (ATC). This automatic temperature compensation system is necessary since the temperature effects on EMF measurements can cause an apparent change in chemical equilibrium. Also the electrode body material is slow to reach thermal equilibrium after it has been transferred from a solution of one temperature to another. This results in drift until equilibrium has been reached.

The practical work has been simplified for K_1 and K_2 determinations by adopting a practice[10,11] which prevents movement of the electrode between its calibration and usage by equilibrating the cell and electrode in dilute HCl containing the weight percent of ethylene glycol for the calculation of $E°$(cell) followed by addition of stock solutions containing the acid ligands of the required wt. % of ethylene glycol. This is preferable to a technique[12,13] of transferring the glass electrode from an HCl solution to an acid ligand solution followed by extrapolation of timed readings to compensate for any EMF drifts. This procedure is considerably faster than that required with a Pt/H2 electrode cell where each measurement necessitates refilling with a fresh buffer solution. Moreover several values of K_1 and K_2 could be computed from a single run. The buffer compositions were taken as [H_2L]: [Na_2 CO_3] = 3: 1 for K_1 work and 1.2: 1 for K_2 work (H_2 L represent dicarboxylic acid). About 230 g of the required wt. % ethylene glycol (to ± 0.1 g) was weighed into the cell together with sufficient diluted HCl (≅ 0.035 m) containing the required wt.% of ethylene glycol to make 0.0015 to 0.0025 m HCl (addition by weighing pipette ±0.1 mg). With the electrode in position, the cell was equilibrated at the desired temperature (± 0.1 °C), this could take up to three hours. The HCl solution was then given a short stir (≅ 5s) by fitted microstirrer and left to settle until the EMF was constant (≅ 30 min). Up to six additions of stock buffer were then added by weighing pipette. Each addition was stirred and EMF of the cell then monitored to constancy . The time needed could vary from ≅ 1h for the first addition for a K_2 series (the point of greatest EMF change) down to ≅ 15 min for latter additions and for all K_1 series.

In the present work pK_1 and pK_2 values of oxalic acid have been determined in ethylene glycol-water media of varying solvent compositions (0 – 50 wt% ethylene glycol) within the temperature range (30 – 60 ° C).The expressions used for calculating K_1 and K_2 are,

$$K_1 = [\ H^+]\ [HL^-]\ \gamma_{H^+}\ \gamma_{HL}^-/[H_2L] \quad (1)$$

$$K_2 = [H^+]\ [L^{2-}]\ \gamma_L{}^{2-}/[HL^-] \quad (2)$$

$$K_{NaL^-} = [Na^+]\ [L^-]\ \gamma_{L^-}/[NaL^-] \quad (3)$$

$$-\log \gamma i = AZ_i^2\ [I^{1/2}/(1 + BI^{1/2}) - QI] \quad (4)$$

$$E_{(cell)} = E\ °_{(cell)} - k`\ \log\ (\ [H^+]\ [Cl^-]\ \gamma_{H^+}\ \gamma Cl^-) \quad (5)$$

$$(k` = 2.3026\ RT/F)$$

Where I and γ – represent ionic strength and activity coefficient, repectively ($\gamma_{H_2L} = 1$). The Debye-Huckel constant (A)

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was calculated for each temperature and each solvent composition while the constants "B" and "Q", the values of which were taken as 1.3 and 0.3, respectively, according to the data of Monk.[10] Firstly $E°_{(cell)}$ was calculated from Eqns (4) and (5) by knowing $E_{(cell)}$ of the diluted HCl solution (I = HCl). If the stoichiometric molal concentrations of HCl, H_2L and Na_2CO_3 are m_1, m_2 and m_3, respectively, the following equations are used (with Eqns [(1) – (5)] for calculating K_1.

$$[H_2L] = m_1 + m_2 - 2m_3 - [H^+] + [L^{2-}] + [NaL^-] \quad (6)$$

$$[HL^-] = m_2 - [H_2L] - [L^{2-}] - [NaL^-] \quad (7)$$

Approximate values of $[H^+]$ on the addition of buffer solution were calculated from Eqns (4) and (5) with $I = m_1$ followed by use of Eqns (6) and (7) with $[L^{2-}] = 0$ and $[NaL^-] = 0$ in the first cycle. The subsequent value of I was used to recalculate $[H^+]$ followed by calculation of $[L^{2-}]$ via Eqn (2) with published or estimated values of K_2. $[Na^-]$ was calculated from Eqn (3) using $K_{NaL} = 0.2$. If present estimates of K_2 were significantly different, the calculations were repeated until the difference between successive values of $[H^+]$ agreed to $\Delta [H] < 1 * 10^{-9}$ m, K_1 was then obtained from Eqns (1) and (4). For K_2, $[H^+]$ was calculated as described above and then by applying Eqns (8) and (9).

$$[HL^-] = m_1 + 2m_2 - 2m_3 - [H^+] - 2[H_2L] \quad (8)$$

$$[L^{2-}] = m_2 - [H_2L] - [HL^-] - [NaL^-] \quad (9)$$

Table 1 pK_1 and pK_2 values of oxalic acid in ethylene glycol–water mixture, and dielectric constant (D) at different temperatures

Wt/%	T/°C	30	40	50	60
0	pK1	1.31±0.03	1.29±0.02	1.21±0.01	1.16±0.01
	pK2	4.31±0.06	4.34±0.03	4.36±0.05	4.37±0.03
	D	77.86	73.12	69.82	66.62
10	pK1	1.61±0.07	1.53±0.08	1.37±0.07	1.26±0.04
	pK2	4.47±0.09	4.60±0.11	4.83±0.10	5.18±0.11
	D	75.10	70.29	67.40	63.92
20	pK1	1.99±0.02	1.86±0.04	1.53±0.05	1.31±0.08
	pK2	4.73±0.11	4.95±0.16	5.31±0.12	5.70±0.07
	D	71.3	67.52	64.5	61.20
30	pK1	2.03±0.02	1.96±0.07	1.80±0.05	1.66±0.01
	pK2	5.01±0.07	5.20±0.01	5.41±0.02	5.75±0.09
	D	68.40	64.51	62.30	58.37
40	pK1	2.34±0.12	2.09±0.11	1.94±0.05	1.88±0.07
	pK2	5.21±0.05	5.42±0.01	5.61±0.09	5.90±0.08
	D	65.70	61.56	59.28	55.48
50	pK1	2.48±0.08	2.20±0.01	2.16±0.02	1.97±0.07
	pK2	5.29±0.09	5.57±0.11	5.68±0.12	6.02±0.21
	D	62.40	58.25	55.20	52.30

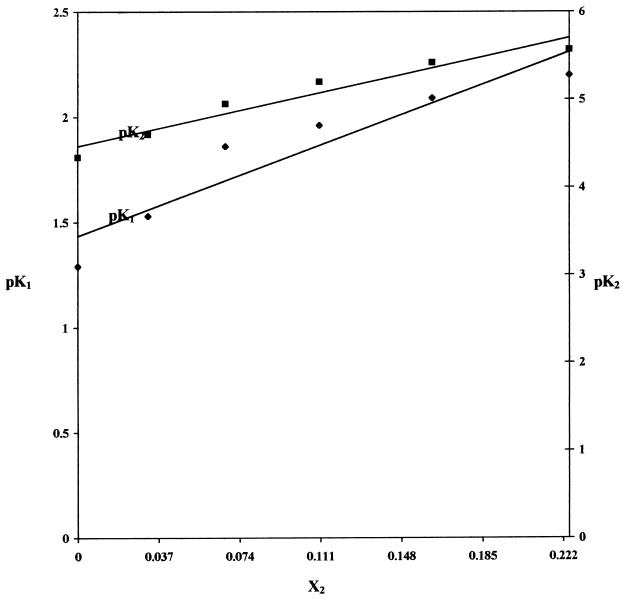

Fig. 1 Variation of pK_1 and pK_2 with the mole fraction of ethylene glycol for oxalic acid at 40°C.

Table 2 $\Delta pK_{1,2}$ values in different solvent composition for some dicarboxylic acids at 45°C

Wt/%		Phthalic	Tartaric	Succinic	Malonic	Malic	Maleic
10	ΔpK_1	0.00	0.05	0.11	0.12	0.12	0.08
	ΔpK_2	0.16	0.29	0.13	0.17	0.14	0.21
20	ΔpK_1	0.12	0.21	0.21	0.23	0.22	0.12
	ΔpK_2	0.17	0.05	0.24	0.33	0.22	0.32
30	ΔpK_1	0.23	0.35	0.35	0.34	0.35	-
	ΔpK_2	0.52	0.12	0.38	0.49	0.41	0.67
40	ΔpK_1	0.35	0.49	-	0.44	0.48	0.32
	ΔpK_2	0.88	0.36	0.54	0.65	0.5	0.95
50	ΔpK_1	0.43	0.59	0.55	0.51	0.53	0.40
	ΔpK_2	1.03	0.4	0.63	0.74	0.59	1.07

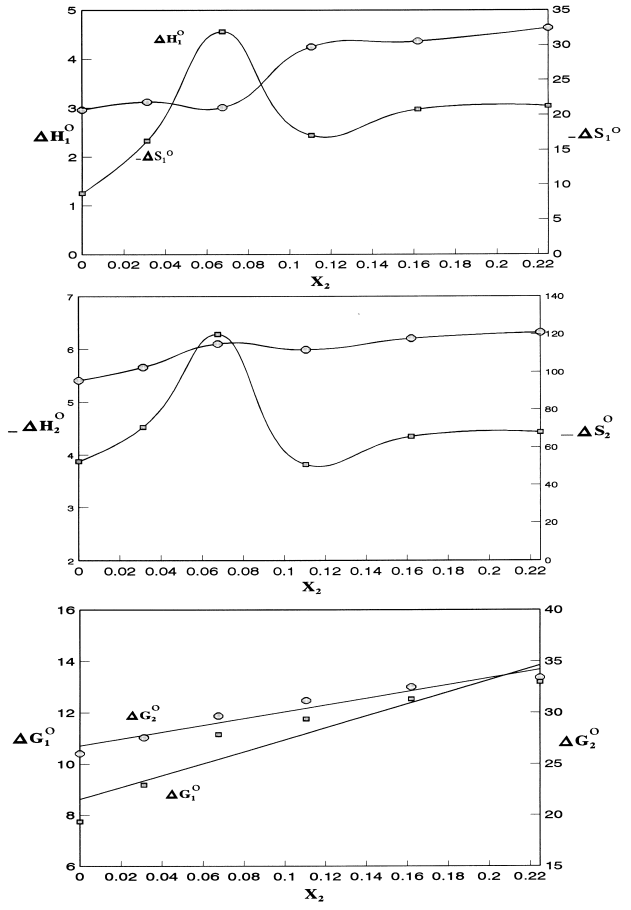

Fig. 2 Variation of DH°, DG° and DS with the mole fraction of ethylene glycole for oxalic acid at 40°C.

With $[H_2 L] = 0$ and $[NaL^-] = 0$ in the first cycle followed by the use of Eqns (1) and (3) for calculating $[H_2 L]$ and $[NaL^-]$, respectively. K_2 was calculated from Eqns (2) and (4) when the difference between two successive values of $[H^+]$ agreed to $\Delta[H] < 1 \times 10^{-9}$m. All computations were made by means of BASIC computer programs. The extrapolated K_1 and K_2 values at zero ionic strength were obtained from the linear least mean square plots of K_1 (or K_2) versus ionic strength.[10,11] The computed pK_1 and pK_2 values at zero ionic strength for different solvent compositions and temperatures with their dielectric constant are shown in Table 1, from which can be readily seen the influence of the composition of the medium on the first and second dissociation constants. The dissociation constant of a weak uncharged acid of the H2L type, expressed by a process involving a net increase in solvated ions, is sensitive to changes in the macroscopic dielectric constant (D) of the medium[14] and with solvents.

The pK_1 and pK_2 values obtained in different solvent mixtures for oxalic acid were found to be linearly correlated with the mole fraction of ethylene glycol (X_2), Fig. 1, the correlation takes the form

$$pK_{1or2} = pK^w + A\ X_2$$

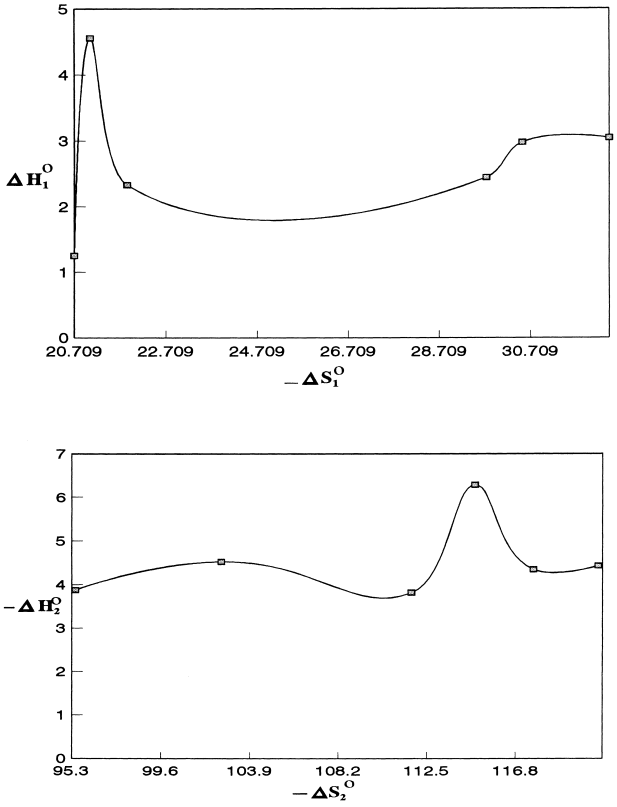

Fig. 3 Isoequilibrium plots for the first and second dissociation reactions of oxalic acid at 40°C.

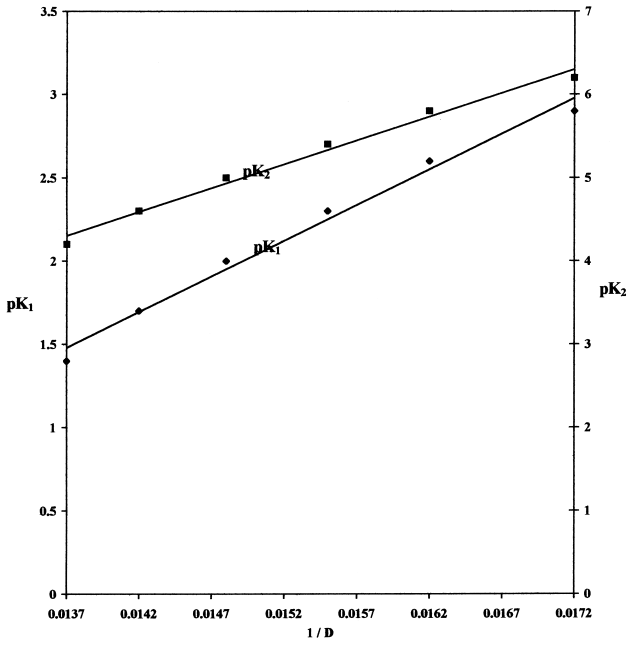

Fig. 4 Variation of pK_1 and pK_2 with D^{-1} at 40°C.

Table 3 Thermodynamic parameters $\Delta H°$, $\Delta G°$ and $\Delta S°$ for the first and second ionization constants in different solvent compositions and at different temperatures ($\Delta H°$, $\Delta G°$ in k/j/mol and $\Delta S°$ in j/mol/k).

Wt/%	T°C	30	40	50	60	T/°C	30	40	50	60
0	$\Delta H_1°$	1.25±0.01	1.25±0.01	1.25±0.01	1.25±0.01	$\Delta H_2°$	3.88±0.02	3.88±0.02	3.88±0.02	3.88±0.02
	$\Delta G_1°$	7.26±0.06	7.74±0.06	7.49±0.06	7.40±0.06	$\Delta G_2°$	25.04±0.11	26.02±0.12	26.98±0.12	27.89±0.12
	$-\Delta S_1°$	19.8±0.2	20.7±0.2	19.3±0.2	18.5±0.2	$-\Delta S_2°$	95.3±0.37	95.5±0.40	95.5±0.40	95.4±0.40
10	$\Delta H_1°$	2.33±0.14	2.33±0.14	2.33±0.14	2.33±0.14	$\Delta H_2°$	4.52±0.27	4.52±0.27	4.52±0.27	4.52±0.27
	$\Delta G_1°$	9.35±0.80	9.17±0.8	8.48±0.9	8.04±0.9	$\Delta G_2°$	25.95±1.6	27.58±1.6	29.89±1.7	33.04±1.7
	$-\Delta S_1°$	23.2±2.7	21.9±2.7	19.0±2.8	17.1±2.8	$-\Delta S_2°$	100.5±5.4	102.5±5.4	106.5±5.3	112.8±5.3
20	$\Delta H_1°$	4.56±0.27	4.56±0.27	4.56±0.27	4.56±0.27	$\Delta H_2°$	6.28±0.37	6.28±0.37	6.28±0.37	6.28±0.37
	$\Delta G_1°$	11.55±1.6	11.15±1.6	9.47±1.7	8.36±1.7	$\Delta G_2°$	27.46±2.1	29.68±2.1	32.86±2.2	36.36±2.2
	$-\Delta S_1°$	23.1±5.4	21.06±5.4	15.2±5.3	11.4±5.3	$-\Delta S_2°$	111.3±7.0	114.8±7.0	121.1±6.90	127.9±6.90
30	$\Delta H_1°$	2.44±0.14	2.44±0.14	2.44±0.14	2.44±0.14	$\Delta H_2°$	3.82±0.22	3.82±0.22	3.82±0.22	3.82±0.22
	$\Delta G_1°$	11.79±0.80	11.75±0.8	11.14±0.9	10.59±0.9	$\Delta G_2°$	29.081±1.3	31.18±1.3	33.47±1.4	36.68±1.4
	$-\Delta S_1°$	30.9±2.7	29.7±2.7	26.9±2.8	24.5±2.8	$-\Delta S_2°$	108.5±4.40	111.8±4.40	115.4±4.39	121.6±4.39
40	$\Delta H_1°$	2.97±0.18	2.97±0.18	2.97±0.18	2.97±0.18	$\Delta H_2°$	4.35±0.25	4.35±0.25	4.35±0.25	4.35±0.25
	$\Delta G_1°$	13.58±1.0	12.53±1.0	12.00±1.1	11.99±1.1	$\Delta G_2°$	30.24±1.5	32.49±1.5	34.71±1.6	37.64±1.6
	$-\Delta S_1°$	35.1±3.4	30.5±3.4	27.9±3.5	27.1±3.5	$-\Delta S_2°$	114.1±5.02	117.7±5.02	120.9±5.01	126.0±5.01
50	$\Delta H_1°$	3.04±0.18	3.04±0.18	3.04±0.18	3.04±0.18	$\Delta H_2°$	4.43±0.26	4.43±0.26	4.43±0.26	4.43±0.26
	$\Delta G_1°$	14.40±1.0	13.19±1.0	13.37±1.1	12.57±1.1	$\Delta G_2°$	30.71±1.5	33.39±1.5	35.14±1.7	38.40±1.7
	$-\Delta S_1°$	37.5±3.4	32.4±3.4	31.9±3.5	28.6±3.5	$-\Delta S_2°$	115.9±5.02	120.8±5.02	122.5±5.32	128.6±5.32

A, is the slope. From this correlation the pK_1 and pK_2 of oxalic acid in ethylene glycol–water mixture containing up to 50 wt % of the organic solvent can be predicted. The strength of an acid in a particular mixed solvent depends on many factors. However, if an acid H_2L is transferred from water into non-aqueous solvent it will be weakened or strengthened by a constant amount[15, 16] that is $\Delta pK_{1or2}=pK^s_{1or2} - pK^w$. Table 2 contains the ΔpK_{1or2} values of some dicarboxylic acids in ethylene glycol–water mixed solvents[17,18]. The similarity of ΔpK_1, for these acids at each composition of solvent means that the dicarboxylic acids are weakened by an approximately constant amount regardless of acid strength. If this finding is extrapolated to other dicarboxylic acid, it can be deduced from this final Eqn. that ΔpK_1 values for a dicarboxylic acid in water – ethylene glycol mixtures can be predicted provided that pK^w is known. This approximate rule for the calculation of pK values is very useful in non-aqueous titrimetry because once the pK_{1or2} values of a dicarboxylic acids are known, valuable information concerning titration can be obtained.[15]

The thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ of dissociation reactions were computed from the well known thermodynamic relations. $\Delta H_1°$ and $\Delta H_2°$ were obtained from the Vant Hoff plots, they may be treated as sensibly constant over the temperature range covered, Table 3 shows these thermodynamic functions for both first and second dissociation reactions with their respective estimates of errors. $\Delta G_1°$and $\Delta G_2°$ have positive values which indicate the preferential stabilisation of H_2L in the first dissociation process and of the species HL^- in the second dissociation process by the mixed solvent. $\Delta G_1°$and $\Delta G_2°$ increase with increasing organic solvent content due to the increase of the electrostatic free energies of the ions produced in the dissociation process due to the decrease of D. The standard entropy of dissociation in most compositions becomes steadily more negative with increasing the ethylene glycol content[19] because the ethylene glycol–water mixtures are less structured than pure water, hence species such as H^+, HL and L^2 will orient solvent molecules to a greater extent in ethylene glycol–water media giving more negative entropy of dissociation values. Non-linear plots were obtained from the variation of $\Delta S_{1,2}°$ and $\Delta H_{1,2}°$ with the mole fraction of ethylene glycol (X_2) Fig. 2, which is a criterion of specific solvation of the species produced through the dissociation processes. The profile of $\Delta H°$ and $\Delta S°$ – mole fraction (X_2) curves predicts that a compensation effect must lie in terms of solute – solvent interactions.

An extrathermodynamic analysis of the obtained results has been examined in the light of $\Delta H°$–$\Delta S°$ relationship Fig. 3 which give a non-linear relation attributed to the complexity of $\Delta H°$ and $\Delta S°$ variation with the mole fraction of the organic solvent and it reflect an appreciable "shielding effect"[20] exerted by the solvent on the properties of acid.

The quantitative explanation of the medium effect on pK_a can be easily described by Born's equation[21] which predicts a linear relationship between pK_{1or2} and $1/D$ Fig. 4, in which the change in pKs are attributed to electrostatic phenomena while the non-electrostatic solute–solvent interactions remain constant, regardless of the solvent composition.

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