The heat of mixing of sodium carbonate and sodium bicarbonate aqueous solutions and its temperature dependence [1]

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Abstract

Heats of mixing of Na_2CO_3 and $NaHCO_3$ aqueous solutions, of the same molal ionic strength, were measured in the 0.02–1.2 m (molality) range and at 298 K using a flow-mix microcalorimetric cell. The most concentrated solutions, 0.4 m Na_2CO_3 and 1.2 m $NaHCO_3$, were mixed at 298, 308, 318, and 328 K; the maximum heat of mixing value was obtained at 308 K. The results are interpreted in terms of the solute–water structural properties.

INTRODUCTION

Many systems of economic importance and scientific interest, such as sea water, biological fluids and metal ion complexes in solutions, contain mixtures of electrolytes [1]. The considerable attention that aqueous electrolyte solutions have received is mostly stimulated by the need to develop an efficient and relatively inexpensive method of converting sea water to potable water [2].

In recent years, there has been great interest in the thermodynamic properties of aqueous solutions at higher temperatures, which is important for an understanding of hydrothermal mineral formation, geothermal brines and corrosion at high temperatures [3].

It is well known [1] that the measurement of the heats of mixing of electrolyte solutions is an excellent way to study the interactions of ions in aqueous solutions. In fact, the heats of mixing are due primarily to specific ion interactions which are the result of ion–water structure interactions [4]. Because water structure is strongly temperature dependent, the temperature dependence of the heats of mixing should shed considerable light on the role that water plays in determining the nature of the specific ion interactions on mixing [2].

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Detailed work carried out in the field of flow calorimetry has shown that flow calorimeters could be used to study the very small heat effects that result from the mixing of solutions with great sensitivity and speed, both at room and higher temperatures [5].

The flow-mix measuring cell of our Thermometric (LKB) multichannel microcalorimeter has already been found [6] to be suitable for the measurement of heats of mixing at 298 K. Because of the great importance of bicarbonate and carbonate ions in natural water systems we have continued our work by measuring the heats of mixing of Na_2CO_3 and $NaHCO_3$ aqueous solutions of the same molal ionic strength in the $0.02–1.2\ m$ range. In an attempt to understand the nature of the specific ions interactions upon mixing, we have examined the heat of mixing temperature dependence in the 298–328 K region.

EXPERIMENTAL

Reagent grade $NaHCO_3$ (Merck) was thermally pre-treated at 383 K for 24 h, while the reagent grade $Na_2CO_3 \cdot 10H_2O$ was used without previous treatment. All the solutions were prepared with freshly boiled, doubly distilled water.

The upper solution concentration limit ($1.2\ m$) was found to be near the less soluble component saturation, while the lower limit ($0.02\ m$) was defined by the calorimeter sensitivity.

We observed that the calorimetric response was irregular in shape whenever the solutions were older than approximately two weeks. We assume that this irregularity is a consequence of hydrolysis of the solutions and, in order to suppress it, each mixing experiment was performed with freshly prepared solutions.

The molality of the solutions was checked by titration with a standard $0.1\ m$ HCl solution. The solutions mixed were approximately the same molal ionic strength.

Mixing experiments were performed in the flow-mix cell of the Thermometric (LKB) multichannel microcalorimeter described previously [6]. Calibration was performed by an electrical heater in the flow cell.

The solutions were introduced into the flow-mix cell by a pair of microperpex peristaltic pumps, previously calibrated with the same solutions. Different fractions of the salt solutions to be mixed were obtained by varying the flow rates, in the range 2–10 ml, of both pumps.

The solution densities were measured by an AP Paar calculating density meter, model DMA 55.

During the experiment the periodical appearance of air bubbles at 328 K disturbed the measurement. Thus, the measurements were not continued at higher temperatures.

RESULTS AND DISCUSSION

The heat of mixing values, each calculated as a mean value of three experimental runs, are summarized in Tables 1–7. The uncertainty interval, calculated as twice the standard deviation of the mean value, was not greater than 8%.

The experimental data were fitted to the equation [1, 2, 4, 7–13]

$$\Delta_m H(\text{J/kg } H_2O) = y_A y_B I^2 (RTh_0^I + (y_B - y_A)RTh_1^I$$
$$+ (y_B - y_A)^2 RTh_2^I + \ldots) \tag{1}$$

where y_A is the ionic strength fraction of salt A (Na_2CO_3), y_B is the ionic strength fraction of salt B ($NaHCO_3$), I is the molal ionic strength of the salt solutions, and RTh_0^I, RTh_1^I, etc., are the parameters that describe the mixing. The h coefficients have the superscript I to indicate that the mixing process takes place at a constant ionic strength. The h_0 coefficient is the magnitude of interaction, and h_1 is the measure of asymmetry from the quadratic relation with respect to the ionic strength fraction. The values of parameters which fit the experimental data best, with the standard deviation as an uncertainty interval, are given in Table 8.

The heat of mixing values $\Delta_m H$ obtained experimentally for different salt solution ionic strengths, as a function of the ionic strength fraction of Na_2CO_3 (Tables 1–4) at 298 K are represented by the symbols in Fig. 1. The theoretical curves, obtained using eqn. (1), are depicted by solid lines. The Na_2CO_3 ionic strength fraction at the maximum heat of mixing attained for each salt solution ionic strength (Fig. 1) y_A^{max} is related to the salt molality m_A in Fig. 2. The heat of mixing temperature dependence for the salt solution pair 0.4 m Na_2CO_3–1.21 m $NaHCO_3$ (Tables 1, 5–7) is

TABLE 1

Heats of mixing of 0.40 m Na_2CO_3 and 1.21 m $NaHCO_3$ aqueous solutions of the same molal ionic strength ($I = 1.21$) at 298 K

y_A	y_B	$\Delta_m H$ in (J/kg H_2O)	$\Delta_m H$ in (J/mol $Na_2CO_3 \cdot 10\ H_2O$)
0.06	0.94	90.48 ± 1.14	1405 ± 18
0.11	0.89	106.9 ± 1.0	962.6 ± 8.5
0.16	0.84	125.3 ± 0.6	855.6 ± 4.6
0.20	0.80	136.0 ± 1.6	780.5 ± 9.2
0.24	0.76	136.8 ± 0.5	696.0 ± 2.8
0.28	0.72	118.6 ± 6.4	541.5 ± 29.1
0.34	0.66	101.1 ± 2.8	408.8 ± 11.2
0.44	0.56	74.53 ± 0.80	262.3 ± 2.8
0.61	0.39	31.01 ± 1.15	92.94 ± 3.42

TABLE 2

Heats of mixing of $0.20\ m$ Na_2CO_3 and $0.60\ m$ $NaHCO_3$ aqueous solutions of the same molal ionic strength ($I = 0.60$) at 298 K

y_A	y_B	$\Delta_m H$ in ($J/kg\ H_2O$)	$\Delta_m H$ in ($J/mol\ Na_2CO_3 \cdot 10\ H_2O$)
0.08	0.92	35.36 ± 1.72	1200 ± 59
0.14	0.86	54.28 ± 0.74	1069 ± 15
0.20	0.80	75.36 ± 0.55	1127 ± 10
0.25	0.75	79.32 ± 4.65	997.4 ± 58.6
0.29	0.71	83.08 ± 1.05	926.4 ± 11.7
0.34	0.66	84.43 ± 0.58	845.3 ± 5.8
0.41	0.59	81.75 ± 0.00	725.2 ± 0.0
0.51	0.49	72.15 ± 1.31	557.9 ± 10.1
0.67	0.33	49.75 ± 0.89	328.0 ± 6.0

TABLE 3

Heats of mixing of $0.12\ m$ Na_2CO_3 and $0.36\ m$ $NaHCO_3$ aqueous solutions of the same molal ionic strength ($I = 0.36$) at 298 K

y_A	y_B	$\Delta_m H$ in ($J/kg\ H_2O$)	$\Delta_m H$ in ($J/mol\ Na_2CO_3 \cdot 10\ H_2O$)
0.08	0.92	16.60 ± 1.43	922.5 ± 79.8
0.14	0.86	18.51 ± 1.26	598.0 ± 40.6
0.20	0.80	22.83 ± 0.38	560.6 ± 9.6
0.25	0.75	25.74 ± 1.25	532.3 ± 25.9
0.29	0.71	27.94 + 0.67	512.9 ± 12.3
0.34	0.66	26.89 ± 0.34	443.5 ± 5.7
0.41	0.59	25.39 ± 1.09	371.8 ± 16.4
0.51	0.49	20.21 ± 1.55	258.1 ± 19.8
0.67	0.33	15.17 ± 1.05	165.5 ± 11.5

TABLE 4

Heats of mixing of $0.07\ m$ Na_2CO_3 and $0.20\ m$ $NaHCO_3$ aqueous solutions of the same molal ionic strength ($I = 0.20$) at 298 K

y_A	y_B	$\Delta_m H$ in ($J/kg\ H_2O$)	$\Delta_m H$ in ($J/mol\ Na_2CO_3 \cdot 10\ H_2O$)
0.08	0.92	3.60 ± 0.11	329.3 ± 9.9
0.16	0.84	6.70 ± 0.37	356.8 ± 19.5
0.22	0.78	7.75 ± 0.13	314.1 ± 5.2
0.27	0.73	8.99 ± 0.55	307.0 ± 19.0
0.32	0.68	8.51 ± 0.31	258.0 ± 9.5
0.37	0.63	6.11 ± 0.07	166.7 ± 1.9
0.44	0.56	6.29 ± 0.31	152.3 ± 7.6
0.54	0.46	5.84 ± 0.47	123.5 ± 9.9
0.70	0.30	3.64 ± 0.25	65.87 ± 4.61

TABLE 5

Heats of mixing of 0.40 m Na_2CO_3 and 1.21 m $NaHCO_3$ aqueous solutions of the same molal ionic strength ($I = 1.21$) at 308 K

y_A	y_B	$\Delta_m H$ in (J/kg H_2O)	$\Delta_m H$ in (J/mol $Na_2CO_3 \cdot 10 H_2O$)
0.08	0.92	87.15 $\pm$ 0.85	1539 $\pm$ 15
0.14	0.86	153.2 $\pm$ 0.0	1562 $\pm$ 0
0.20	0.80	177.1 $\pm$ 2.0	1366 $\pm$ 15
0.25	0.75	188.7 $\pm$ 0.0	1222 $\pm$ 0
0.29	0.71	189.8 $\pm$ 3.2	1087 $\pm$ 18
0.34	0.66	163.6 $\pm$ 9.3	839.8 $\pm$ 47.7
0.41	0.59	156.1 $\pm$ 6.4	708.0 $\pm$ 29.1
0.51	0.49	137.5 $\pm$ 0.8	541.8 $\pm$ 3.1
0.67	0.33	92.34 $\pm$ 4.18	308.7 $\pm$ 14.0

TABLE 6

Heats of mixing of 0.40 m Na_2CO_3 and 1.21 m $NaHCO_3$ aqueous solutions of the same molal ionic strength ($I = 1.21$) at 318 K

y_A	y_B	$\Delta_m H$ in (J/kg H_2O)	$\Delta_m H$ in (J/mol $Na_2CO_3 \cdot 10 H_2O$)
0.08	0.92	58.65 $\pm$ 0.88	869.8 $\pm$ 13.0
0.14	0.86	80.59 $\pm$ 2.00	689.9 $\pm$ 17.2
0.20	0.80	88.28 $\pm$ 3.73	571.2 $\pm$ 24.1
0.25	0.75	92.80 $\pm$ 1.80	503.4 $\pm$ 9.7
0.30	0.70	91.29 $\pm$ 1.44	438.9 $\pm$ 3.8
0.34	0.66	92.18 $\pm$ 0.00	395.9 $\pm$ 0.0
0.41	0.59	87.77 $\pm$ 3.13	332.9 $\pm$ 11.9
0.51	0.49	79.27 $\pm$ 3.62	261.0 $\pm$ 11.9
0.68	0.32	65.04 $\pm$ 1.87	181.5 $\pm$ 5.2

TABLE 7

Heats of mixing of 0.40 m Na_2CO_3 and 1.21 m $NaHCO_3$ aqueous solutions of the same molal ionic strength ($I = 1.21$) at 328 K

y_A	y_B	$\Delta_m H$ in (J/kg H_2O)	$\Delta_m H$ in (J/mol $Na_2CO_3 \cdot 10 H_2O$)
0.08	0.92	30.34 $\pm$ 0.95	448.3 $\pm$ 14.0
0.14	0.86	37.20 $\pm$ 2.17	317.2 $\pm$ 18.5
0.20	0.80	47.88 $\pm$ 1.40	308.6 $\pm$ 9.1
0.25	0.75	57.93 $\pm$ 1.20	313.0 $\pm$ 6.5
0.30	0.70	58.84 $\pm$ 0.94	281.1 $\pm$ 4.5
0.35	0.65	56.75 $\pm$ 0.54	242.8 $\pm$ 2.3
0.41	0.59	55.17 $\pm$ 0.35	208.5 $\pm$ 1.3
0.51	0.49	48.82 $\pm$ 1.42	160.1 $\pm$ 1.4
0.68	0.32	33.64 $\pm$ 0.48	93.48 $\pm$ 1.34

TABLE 8

Parameters describing the mixing of Na_2CO_3 and $NaHCO_3$ aqueous solutions of the same molal ionic strength I at temperature T

I	T/K	RTh_0^1 in (J kg mol^{-2})	RTh_1^1 in (J kg mol^{-2})	RTh_2^1 in (J kg mol^{-2})
1.21	298	141.4 ± 13.8	352.8 ± 56.7	615.1 ± 103.4
0.60	298	1701 ± 26	1362 ± 69	–
0.36	298	1291 ± 61	1140 ± 193	767 ± 407
0.20	298	1220 ± 102	1290 ± 294	1076 ± 657
1.21	308	373.8 ± 16.6	389.5 ± 52.8	366.0 ± 111.3
1.21	318	213.1 ± 4.1	116.5 ± 12.4	286.9 ± 16.5
1.21	328	140.3 ± 4.0	116.9 ± 10.7	–
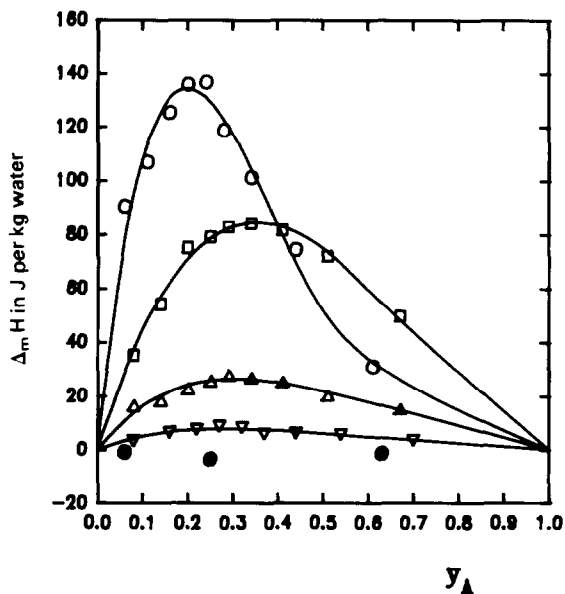
Fig. 1. The heat of mixing $\Delta_m H$ as a function of the ionic strength fraction of Na_2CO_3 (y_A) at 298 K: $\bigcirc$, 0.40–1.21 m; $\square$, 0.20–0.60 m; $\triangle$, 0.12–0.36 m; $\triangledown$, 0.07–0.20 m; $\bullet$, 0.02–0.06 m. The first number represents molal concentration of Na_2CO_3, and the second refers to $NaHCO_3$.

illustrated in Fig. 3. The maximum heat of mixing values $\Delta_m H^{max}$ for each curve in Fig. 3, versus temperature, T are represented in Fig. 4.

It is well known [8] that ions can be roughly divided into three structural classes: structure breakers, which have a net effect of breaking the water structure around them; electrostrictive structure makers, which order the water molecules by their high electric fields; and hydrophobic structure
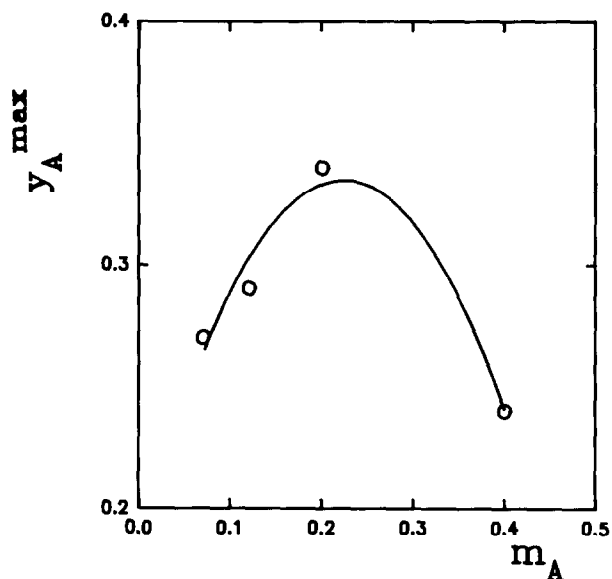
Fig. 2. Na_2CO_3 ionic strength fraction for a maximum heat of mixing y_A^{max} versus Na_2CO_3 solution molality m_A at 298 K; solid line represents the second-power polynomial.

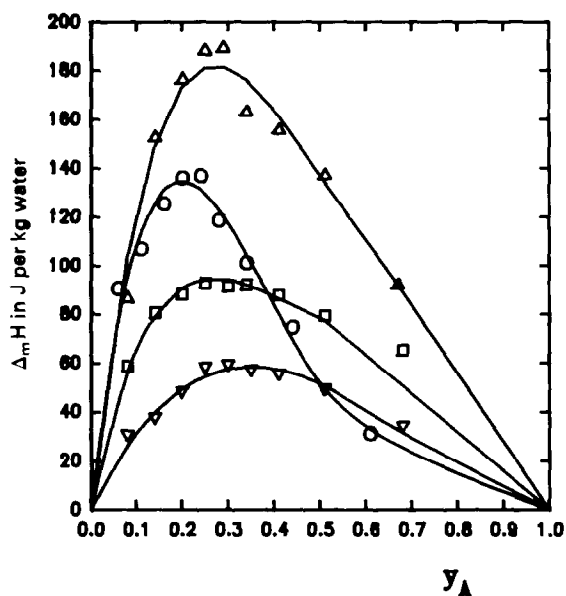Fig. 3. Heats of mixing $\Delta_m H$ of 0.40 m Na_2CO_3 and 1.21 m $NaHCO_3$ as a function of the ionic strength fraction of Na_2CO_3 (y_A) at: $\bigcirc$, 298 K; $\triangle$, 308 K; $\square$, 318 K; and $\triangledown$, 328 K.

makers, which induce more hydrogen bonding in the water near their non-polar surface. The sign of the heat of interaction of like-charged ions can be predicted on the basis of the effect of ions on the water structure. The rule is that two structure-making ions or two structure-breaking ions
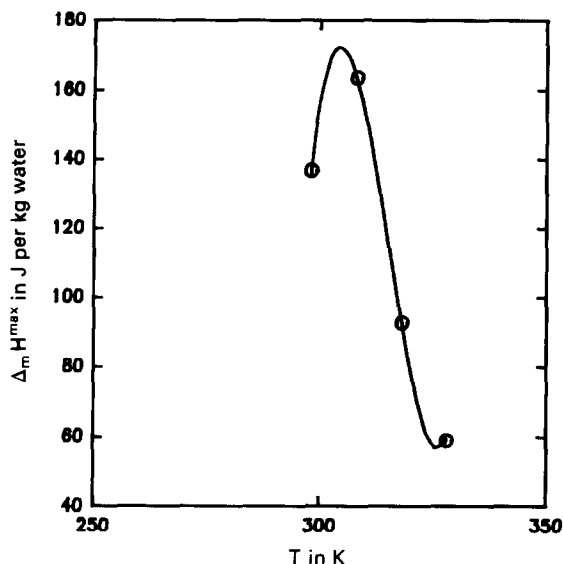
Fig. 4. Maximum heat of mixing $\Delta_m H^{max}$ versus temperature T; the solid line represents the third-power polynomial.

give a positive heat of mixing, whereas mixing a structure maker with a structure breaker gives a negative heat of mixing [9, 10]. The endothermic (positive) heats of mixing obtained upon mixing the Na_2CO_3 and $NaHCO_3$ solutions with a common small, structure-making Na^+ ion [11] are in accordance with the mixing rule mentioned above.

It is obvious from Fig. 1 that the heat of mixing decreases with decreasing solution ionic strength, even becoming negative in the case of mixing $0.02\ m\ Na_2CO_3$ and $0.06\ m\ NaHCO_3$ solutions. Because the mixing of such dilute solutions gave heat values near to zero with an experimental error of about $\pm 30\%$, only three points are presented as an illustration in Fig. 1.

According to Fig. 2, the ionic strength fraction at the maximum heat of mixing y_A^{max} reaches its own maximum value for approximately $0.22\ m\ Na_2CO_3$ solution. The conclusion from Figs. 1 and 2 is that the heat of mixing versus Na_2CO_3 ionic strength fraction curves are similar to the C curve of the Wu classification [12], but are asymmetrical in the opposite direction. The marked skewness of the curves obtained are also confirmed by the high RTh_1 values (Table 8). For common-ion symmetrical mixtures, the coefficient of interaction h_0 is much greater than the asymmetry parameter h_1; but if the heteroions in a common-ion mixture are of a mixed charge type, then the asymmetry coefficient can play a significant role [12]. For charge-symmetric mixtures at constant I, the only terms contributing to skew are triplet interactions of all ions bearing the same charge, while the charge-asymmetric mixtures, such as Na_2CO_3–$NaHCO_3$, all triplets contribute to the skew [13]. As well as the triplet interactions, h_1 is a measure

of opposite-charge pair interactions [12]. We assume that the $Na^+-HCO_3^-$ pair, as well as the $Na^+-Na^+-CO_3^{2-}$ triplet, are the most probable structures formed during the mixing, which explains the high h_1 values obtained. For almost all the curves, even the second-order skew term RTh_2^1 was determined, but with a great uncertainty interval.

It is obvious from Figs. 3 and 4 that the heat of mixing of $0.4\,m$ Na_2CO_3 and $1.2\,m$ $NaHCO_3$ exhibits a maximum at 308 K and then decreases with increasing temperature. Such a temperature dependence has already been observed for $HCl-NaCl$, $LiCl-NaCl$ [2], $NaCl-CsCl$ [4] and n-Pr_4NCl–$NaCl$ [14] mixtures.

The Frank–Evans–Wen [15] structure-making, structure-breaking model for ions in water can be used in an attempt to explain the heat of mixing decrease with increasing temperature. This model assumes that the ions are immediately surrounded by a region of structure-made water (water strongly associated with the ion, i.e. the primary hydration sphere), and then by a region of structure-broken water lying between the structure-made water around the ion and the bulk water. The assumption is that the specific interactions observed upon mixing involve ion–solvent interactions at the interface between the primary hydration sphere and the disordered water in the structure-broken region [2]. It is also suggested that this region is thermally stable in the 298–353 K temperature range for all the ions studied, except for sodium ion [2]. Thus, we can assume that a large number of water molecules in the solution are structured around the Na^+ ion, and that the primary hydration sphere breaks down with increasing temperature, causing the heat of mixing to decrease.

More or less abrupt changes in slopes when various parameters of water and aqueous solutions are plotted as a function of temperature are known as "kinks" [16, 17]. The existence of kinks requires the presence of strongly interacting, cooperating aggregates of water molecules able to undergo some type of order–disorder transformation, such as higher-order phase transitions [16]. As anomalies occur at 288, 303, 318 and 333 K, within one or two degrees of these temperatures, it occurred to us that the heat of mixing maximum near to 308 K (Fig. 4) could be a type of kink. In order to check the result, the heat of mixing measurement at 308 K was carried out twice for some experimental points (Fig. 3). However, in order to confirm the anomaly obtained, it would be necessary to perform the experiment at a few closely spaced temperatures near 308 K.

It is well known [5] that flow calorimeters can be used to study very small heat effects on mixing solutions with great precision, and it is also confirmed [18] that flow calorimetry offers a rapid and precise method of extending thermodynamic measurements on aqueous solutions to high temperatures. Nowadays, flow calorimetric measurements are mostly performed in order to obtain the enthalpies of dilution and heat capacities of electrolyte solutions at temperatures and pressures up to 600 K and 30 MPa [18–30].

Our results confirm that the flow-mix microcalorimetric cell is suitable for direct and precise heat of mixing measurements, but unfortunately up to temperatures not exceeding 353 K. As the temperature limit is determined by the calorimeter construction, the instrument should be modified in order to perform experiments at higher temperatures.

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