

# Evidence for Nonideality in Liquid Mixtures of Hydrogen Chloride and Deuterium Chloride

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The difference between the vapor pressure of liquid hydrogen chloride and that of an approximately equimolar liquid mixture of hydrogen chloride and deuterium chloride has been measured at nine temperatures between 195 and 226 K. The results show that the vapor pressure of this liquid mixture is greater than what would be expected if the solution were strictly ideal, by 72 Pa at 223.35 K and by 34 Pa at 200 K. These pressure differences are between 1 and 2 parts in  $10^4$  of the vapor pressure. The nonideality is also illustrated by the fact that the temperature at which the vapor pressure of hydrogen chloride and that of the liquid mixture are equal is about 0.5 K lower than the temperature (223.35 K) at which pure hydrogen chloride and deuterium chloride have the same vapor pressure. It is difficult to assess what contribution to the nonideality is made by the imperfection of the vapor phase, but reasons are given for believing that the observed effects are primarily a manifestation of nonideality in the liquid phase. These effects correspond to an excess Gibbs energy ( $G^E$ ) for the equimolar mixture of about  $0.25 \text{ J mol}^{-1}$  over the temperature range of the measurements, which is some 3 orders of magnitude smaller than the  $G^E$  values typically found for mixtures of two (nonisotopic) condensed gases.

## 1. Introduction

In a previous paper<sup>1</sup> (which we shall refer to as part 1) we presented vapor pressure results for hydrogen chloride and deuterium chloride obtained with an apparatus that could be used both to measure the absolute vapor pressure of the pure liquids and to determine the difference in the vapor pressures of the two isotopic species at chosen temperatures. We record here the results of measurements of the vapor pressure difference, over a range of 31 K, between pure HCl and an approximately equimolar liquid mixture of HCl and DCl. The purpose of these experiments was to see if any nonideality in the properties of such a mixture could be detected. Nonideality has been definitely discerned in binary isotopic liquid mixtures with much lower boiling points, notably  $\text{H}_2 + \text{D}_2$  and  $^3\text{He} + ^4\text{He}$ , but the liquids in these two systems are of course essentially quantum fluids, and it was expected at the outset that any such behavior in mixtures of HCl and DCl would be on an altogether smaller scale.

## 2. Experimental Section

The specimens of HCl and DCl were the same as those used in the work reported in part 1, wherein information on their preparation and purity will be found. The DCl used to make the mixture contained 1.0% HCl, and allowing for this, the mole fraction of HCl in the mixture used in the present work was 0.4960.

A sample of the mixture was condensed into a small cylindrical platinum vessel in a cryostat of internal volume of about  $0.12 \text{ cm}^3$ , and a sample of pure HCl was condensed into a second similar vessel. The vapor pressure difference between the two samples was measured to 0.01 mmHg on a mercury manometer. Throughout these measurements, made from 195 to 226 K, the surface of each liquid sample was maintained at the same level, corresponding to  $0.05 \text{ cm}^3$  of each liquid. The tubing connecting the platinum vessels with the mercury manometer was of  $\sim 1\text{-mm}$  diameter. As the apparatus had been constructed with the intention of studying pure liquids and not mixtures, no provision had been made for stirring the liquids in the platinum vessels, and the question therefore arises of how far possible failure to establish true equilibrium between the vapor and liquid phases of the mixture in our experiments may cast doubt on the validity of our results as being the true vapor pressure difference between pure HCl and a mixture with  $x(\text{HCl}) = 0.4960$ . In view of the small

TABLE I: Experimental Values of  $\Delta p = p(\text{HCl}) - p(\text{mix})^a$

$T^b/\text{K}$	$\Delta p/\text{kPa}$	$p(\text{HCl})^c/\text{kPa}$	$r(\text{mix})^d$
195.543	0.924	151.173	1.0061
204.304	0.865	233.974	1.0037
207.253	0.801	268.623	1.0030
210.553	0.719	311.978	1.0023
214.252	0.524	366.796	1.0014
215.162	0.552	381.351	1.0014
216.921	0.397	410.739	1.0010
219.200	0.263	451.358	1.0006
226.087	-0.300	592.914	0.9995

<sup>a</sup>  $p(\text{HCl})$  is the vapor pressure of HCl, and  $p(\text{mix})$  is that of the mixture  $0.496(\text{HCl}) + 0.504(\text{DCl})$ . <sup>b</sup> Temperatures are on IPTS-68. <sup>c</sup> Values of  $p(\text{HCl})$  are calculated from the Wagner equation in ref 1. <sup>d</sup>  $r(\text{mix}) = p(\text{HCl})/p(\text{mix})$ .

volume of the platinum vessels, it is highly likely that within these vessels true equilibrium was readily attained. The measurements were made by proceeding from the lowest to the highest temperature, and more of the mixture of the two gases was progressively introduced to maintain the desired constancy of the amount present as liquid. This procedure, coupled with the fact that the platinum vessel and the manometer were connected by a capillary tube, rendered it probable that the composition of the gas in the manometer (the volume of which was about  $15 \text{ cm}^3$ ) was the same throughout, namely that of  $x(\text{HCl}) = 0.4960$ . (The device of preventing attack by a corrosive vapor on the mercury of a manometer by filling the latter with a noncorrosive gas such as nitrogen and making the connection to the vessel containing the corrosive liquid and its vapor with a capillary tube to suppress diffusion is well-known.) We therefore believe that consideration of the consequences of the absence of stirring can be confined to the state of affairs within the platinum vessel. The vapor pressure difference between HCl and DCl reaches its maximum at  $\sim 195 \text{ K}$ .<sup>1</sup> If sufficient of the gas mixture of  $x(\text{HCl}) = 0.4960$  were condensed into the vessel at this temperature to give  $0.05 \text{ cm}^3$  of liquid and  $0.07 \text{ cm}^3$  of vapor in true equilibrium with each other, the mole fraction of HCl in the liquid would differ from 0.4960 by less than 0.0001. The difference in the vapor pressure of the liquid corresponding to a change in  $x(\text{HCl})$  of 0.0001 is only 0.2 Pa, which is about an order of magnitude less than the precision of our pressure measurements. We therefore consider that the

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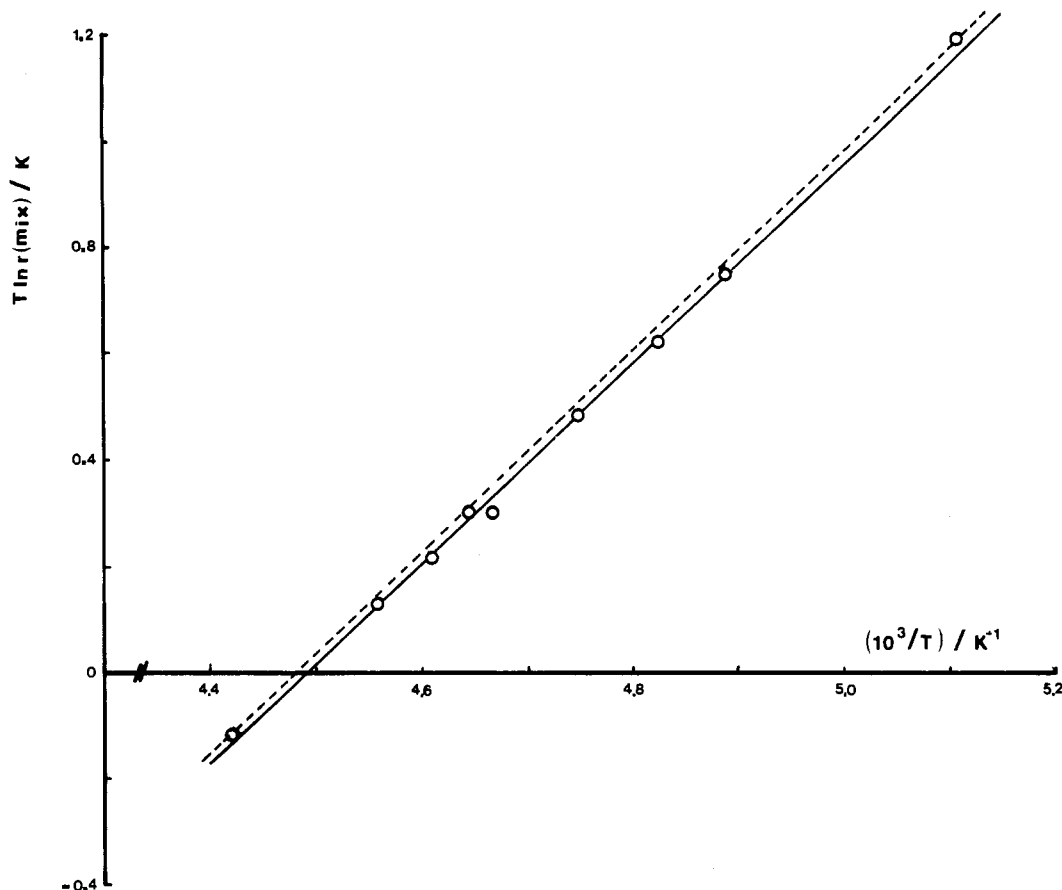


Figure 1. Plot of the experimental values of  $T \ln r(\text{mix})$  against  $T^{-1}$ , where  $r(\text{mix}) = p(\text{HCl})/p(\text{mix})$ . The dashed line represents ideal behavior, being a plot of  $0.504 T \ln r/r$  where  $r = p(\text{HCl})/p(\text{DCl})$ .

vapor pressure results we present below can be regarded as valid for the mixture of the composition stated.

### 3. Results and Discussion

In Table I we give for nine temperatures our measured values of  $\Delta p = p(\text{HCl}) - p(\text{mix})$ , where  $p(\text{HCl})$  and  $p(\text{mix})$  are respectively the vapor pressure of pure liquid HCl and of the mixture. The values of  $p(\text{HCl})$  have been calculated from the Wagner equation for HCl given in part 1. We also record in Table I the values of  $r(\text{mix}) = p(\text{HCl})/p(\text{mix})$ . In part 1, it was shown that the quantity  $T \ln r$ , where  $r$  was the ratio  $p(\text{HCl})/p(\text{DCl})$ , conforms very closely to the equation

$$T \ln r = -A + C/T \quad (1)$$

The same is true of  $T \ln r(\text{mix})$  in the present case, as is shown by Figure 1, in which  $T \ln r(\text{mix})$  is plotted against  $1/T$ . A least-squares fit of eq 1 to the experimental points gives  $A = 8.495$  K and  $C = 1890.6$  K<sup>2</sup>.

Figure 1 can be used to see if our results indicate any nonideality in the HCl + DCl mixture. If we assume for the moment that the vapor phase of the solution is ideal (a matter to which we shall return later), it readily follows that  $T \ln r(\text{mix})$  for a mixture with  $x(\text{DCl}) = 0.5040$  is, to a high degree of approximation, equal to  $0.504 T \ln r/r$  with  $r = p(\text{HCl})/p(\text{DCl})$ . By the use of the data in part 1, this latter quantity has also been plotted in Figure 1 as the dashed line. It will be seen that this is not coincident with the line through the experimental points for the case involving the mixture. Over the whole range covered, the experimental values of  $r(\text{mix})$  are smaller than the ideal values, indicating that the vapor pressure of the solution departs positively from Raoult's law. This departure amounts to 34 Pa ( $\approx 0.25$  mmHg) at 200 K and 72 Pa ( $\approx 0.54$  mmHg) at 223.35 K, the temperature at which (as shown in part 1) the vapor pressures of pure HCl and DCl are equal. These pressure differences, though small (being

only between 1 and 2 parts in  $10^4$  of the vapor pressure) are nevertheless an order of magnitude larger than the precision of the differential vapor pressure measurements.

Particular interest attaches to the temperature 223.35 K, at which  $p(\text{HCl}) = p(\text{DCl})$ . At this temperature (still assuming the vapor to be ideal) the composition of *any* liquid mixture, if ideal, should be identical with that of its vapor. Accordingly, the problems discussed in the preceding section resulting from a possible failure to establish true equilibrium between the vapor and liquid of a known composition then no longer arise. Ideality would therefore require that, at 223.35 K,  $p(\text{mix})$  for *any* mixture should equal  $p(\text{HCl}) (=p(\text{DCl}))$  and that  $T \ln r(\text{mix})$  for the HCl/mixture case should be zero. Figure 1 shows that this is not the case, but the point is made more evident by Figure 2, where the plots of  $T \ln r$  and  $T \ln r(\text{mix})$  against  $1/T$  are shown for the pure liquid pair and the HCl/mixture pair;  $r$  in each case is calculated by using the actual experimental values at the three highest temperatures of  $p(\text{HCl}) - p(\text{DCl})$  (taken from part 1) and of  $p(\text{HCl}) - p(\text{mix})$ . The difference between the temperature at which  $r = 1$  for the two cases is 0.51 K.

The question arises whether the small degree of nonideality our measurements disclose is to be principally attributed to nonideality of the *liquid* phase or to that of the *vapor* phase. To discuss this, we use the following expression for the partial pressure  $p_1$  of component 1 over a binary liquid mixture of components 1 and 2, in which it is assumed that the imperfection of the vapor phase is adequately dealt with in using no virial coefficient higher than the second (which is certainly an acceptable approximation for our present purpose)

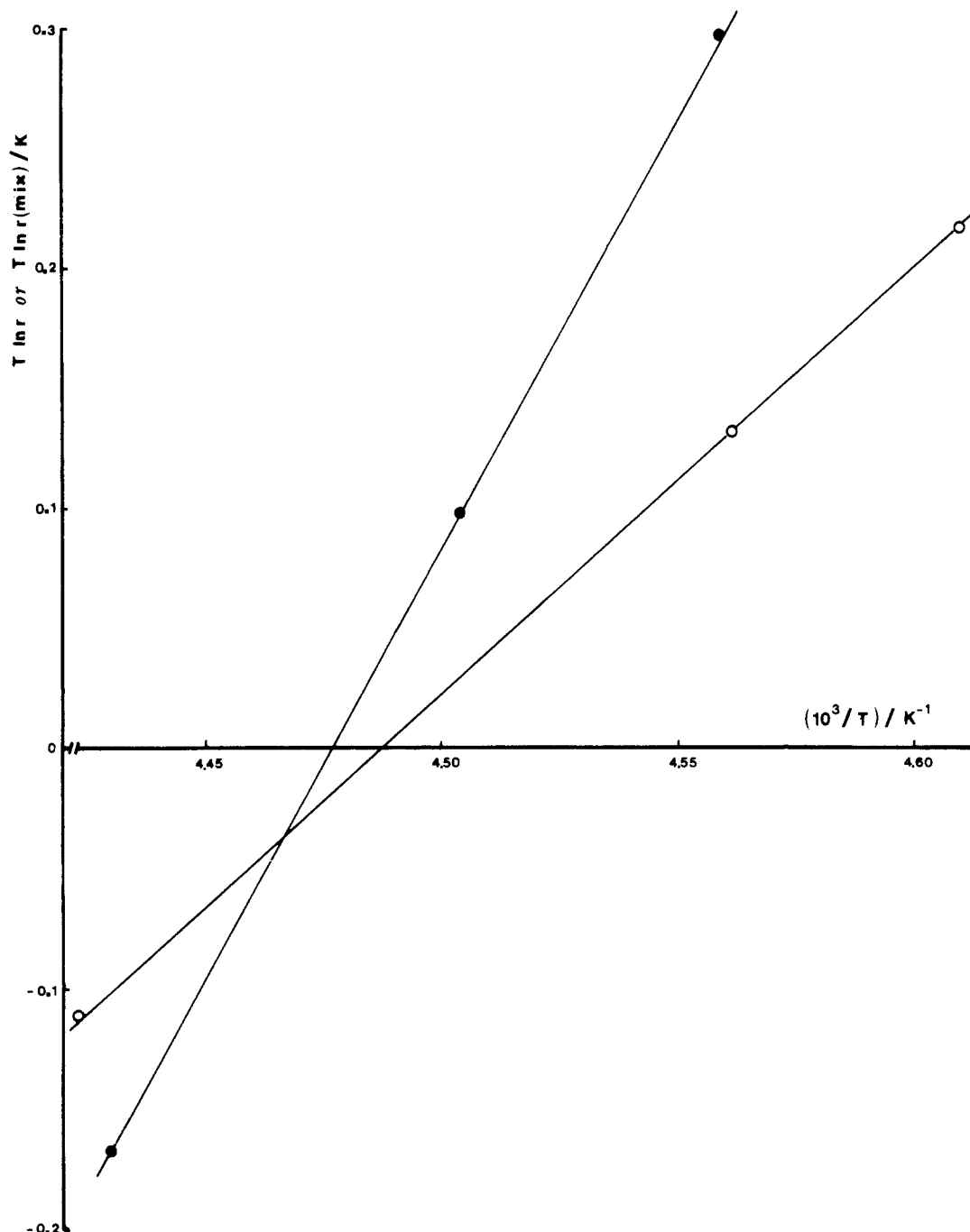
$$p_1 = \gamma_1 x_1 p_1^* X_1 Y_1 \quad (2)$$

where

$$X_1 = \exp[(V_1^* - B_{11})(p - p_1^*)/RT] \quad (3)$$

and

$$Y_1 = \exp[-p y_2^2 \delta_{12}/RT] \quad (4)$$



**Figure 2.** Plot of  $T \ln r$  and  $T \ln r(\text{mix})$  against  $T^{-1}$  between 216 and 226 K. For the full circles,  $r = p(\text{HCl})/p(\text{DCl})$  as calculated from the experimental values of  $p(\text{HCl}) - p(\text{DCl})$ .<sup>1</sup> For the open circles,  $r(\text{mix}) = p(\text{HCl})/p(\text{mix})$ .

$x_1$  and  $\gamma_1$  are the mole fraction and activity coefficient, respectively, of component 1 in the liquid phase,  $p_1^*$  is the vapor pressure of pure 1,  $V_1^*$  is the molar volume of liquid 1,  $B_{11}$  is the second virial coefficient of 1, and  $y_2$  is the mole fraction of component 2 in the vapor phase.  $\delta_{12}$  is given by the equation

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad (5)$$

where  $B_{12}$  is the cross virial coefficient for the interaction of a molecule of 1 with a molecule of 2. A corresponding set of equations obtains for  $p_2$ , the partial pressure of component 2.  $p = p_1 + p_2$  is the total vapor pressure of the mixture.

Schramm and Leuchs<sup>2</sup> determined the second virial coefficients of HCl and DCl from 190 to 300 K and found that they were equal within their experimental error of  $\sim 1 \text{ cm}^3 \text{ mol}^{-1}$ . Values of the molar volumes of liquid HCl and DCl, reported in part 1, are equal to within 0.1%. The effect of gas imperfection is best examined by considering the terms  $X_1$  and  $Y_1$  separately, which we will do at two temperatures, namely, 223.35 and 200 K.

At 223.35 K,  $B$  for the pure gases is  $-296 \text{ cm}^3 \text{ mol}^{-1}$ , and for an equimolar mixture the value of  $X$  for both components is  $1 + 13 \times 10^{-6}$ . The effect of this on  $p$  is only  $\sim 7 \text{ Pa}$ , as compared with the observed value of  $p(\text{actual}) - p(\text{ideal})$  of 72 Pa. At 200 K, at which  $B$  for the pure gases is  $-397 \text{ cm}^3 \text{ mol}^{-1}$ , the effect of the  $X$  term on  $p$  is still only about 1 Pa. The position with regard to the  $Y$  term is less clear, since there are no experimental values for  $\delta_{12}$ . The value of  $B$  for a gaseous mixture in which components 1 and 2 have mole fractions of  $y_1$  and  $y_2$ , respectively, is

$$B = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \quad (6)$$

If  $B_{11}$  and  $B_{22}$  are assumed to be equal, then if  $B$  for an equimolar mixture were to differ from them by only  $0.25 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\delta_{12}$  would be  $-1 \text{ cm}^3 \text{ mol}^{-1}$ . With  $\delta_{12} = -1 \text{ cm}^3 \text{ mol}^{-1}$ ,  $Y_1$  at 223.35 K is  $1 + 72 \times 10^{-6}$ , and the resulting effect of the  $Y$  term for the two components on the total vapor pressure  $p$  would be an increase over the ideal value of 38 Pa, which is comparable with the observed effect. With the same value of  $\delta_{12}$  at 200 K,  $Y_1$  would

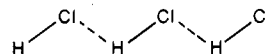
be  $1 + 28 \times 10^{-6}$ , and the effect of this term on  $p$  would now only be about 5 Pa, which is about an order of magnitude smaller than the observed effect at this temperature.

Unfortunately, lack of appropriate data prevents the prediction with any confidence of the value of  $\delta_{12}$ . It is doubtful if the techniques at present available for determining second virial coefficients at lower temperatures are sufficiently refined to allow  $\delta_{12}$  to be determined to better than a few cubic centimeters per mole. However, what evidence there is on second virial coefficients of mixtures of two gases (which are not isotopic forms of the same substance) indicates that  $\delta_{12}$  is usually positive, so that generally the  $Y$  term operates to reduce, and not increase, the total vapor pressure of the mixture. Also, the approximate calculation just presented shows, as is to be expected, that the influence of gaseous imperfection of the vapor pressure falls rather rapidly as the temperature drops, whereas, as may be seen from Figure 1, for solutions of HCl and DCl the observed degree of nonideality appears to be about the same over the temperature range covered by our measurements.

It therefore seems to us that the balance of the evidence favors the conclusion that liquid mixtures of HCl and DCl show a small but definite departure from ideal behavior. If we assume that the  $X$  and  $Y$  terms of eq 2 can both be taken as unity, then the observed values of  $\Delta p$  at 223.35 and 200 K both correspond to a value of the excess Gibbs energy  $G^E$  for the equimolar mixture of about  $0.25 \text{ J mol}^{-1}$ . This is about 3 orders of magnitude less than the  $G^E$  values found for liquefied gas mixtures of nonisotopic components. Thus, for the argon-krypton system,<sup>3</sup> which by ordinary standards is only slightly imperfect,  $G^E$  for the equimolar mixture at 115.8 K is  $85 \text{ J mol}^{-1}$ .

If our conclusion about the nonideality is accepted, attempts to account for it must be based on the small differences between the molecules of HCl and DCl. Because the zero-point energy associated with the intramolecular vibration is greater for HCl than for DCl, the DCl molecule in its vibrational ground state has a slightly shorter bond. Measurements of the polarization of gaseous HCl and DCl led Bell and Coop<sup>4</sup> to conclude that the

dipole moment of DCl exceeds that of HCl by 0.003–0.007 D and that the mean polarizability of HCl is about 0.2% greater than that of DCl. Schramm and Leuchs suggested that the virtual equality of the second virial coefficients of the two gases arises because the differences in polarizability and dipole moment have opposing effects which almost cancel each other. However, more recent estimates of the dipole moments of the two molecules, derived by Kaiser<sup>5</sup> from spectroscopic studies, give HCl the larger moment, Kaiser's values for the molecules in their ground vibrational states being  $\mu(\text{H}^{35}\text{Cl}) = 1.1085 \text{ D}$  and  $\mu(\text{D}^{35}\text{Cl}) = 1.1033 \text{ D}$ . We shall not further consider this matter of the molecular parameters, but we offer one comment that may be relevant in any attempt at a fundamental interpretation of our results. There is indisputable diffraction evidence<sup>6</sup> that the molecules of HCl (and of course of DCl) tend to associate by hydrogen bonding in a zigzag chain:



This association is complete in the low-temperature ordered form of the solids and persists as a form of local order in the high-temperature crystalline modification and also in the liquid state.<sup>7</sup> In either pure HCl or DCl, the internal vibrations of the individual molecules linked in such a chain can operate in phase. But in the mixed chain of HCl and DCl molecules which must exist in a mixture of the two, such synchronized vibrations are no longer possible since the internal vibrational frequencies of HCl and DCl are of course different, being  $2785$  and  $2018 \text{ cm}^{-1}$ , respectively, in the liquid state.<sup>8</sup> This must have an effect, even if small, on the thermodynamic properties of the mixture and might, for example, lead to a tendency for the mixing not to be completely random. Since this tendency is in the direction of the segregation of the two components, one would expect it to favor a nonzero positive  $G^E$ .

Registry No. HCl, 7647-01-0; DCl, 7698-05-7.

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