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Contents

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A Method of Calculating Tunneling Corrections For Eckart Potential Barriers

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A method is presented for the direct calculation of tunneling corrections for unsymmetrical Eckart type potential barriers. It is based on a modified 6-point Gaussian quadrature formula. Accuracy is better than 1 percent over a wide range of tunneling parameter values.

Key words: chemical rate constants; Eckart potential; potential barriers; quantum mechanical tunneling calculations; tunneling corrections.

1. Introduction

The Eckart potential function [1][1] is often used to estimate quantum mechanical tunneling corrections to theoretically determined chemical rate constants. The correction factor Γ^* is defined as the ratio of the quantum mechanical to the classical mechanical barrier crossing rate. It can be expressed [2] as in integral over the energy E,

$$\Gamma^* = \exp(V_1/kT) \int_{E_o}^{\infty} K \exp(-E/kT) dE/kT \tag{1}$$

where V_1 is the height of the potential barrier, and K is the transmission probability for tunneling. K depends on E and three other parameters which are determined by the shape of the barrier and an effective mass for the system. Johnston and Heicklen [3] have evaluated this integral numerically for a number of parameter values. For certain applications their results are inconvenient to use because interpolation is required to get values not tabulated. In view of this, I have devised a simple method which can be used to calculate Γ^* directly, for any set of parameter values within the ranges chosen by Johnston and Heicklen. The method is presented in the form of a small FORTRAN subroutine called TUNL. In the next section, the details of the method are discussed. Following this, the results of a series of comparisons with an accurate calculation are presented. Finally, the subroutine is listed in the Appendix.

2. Derivation of the method

Eckart's potential has the form

$$\begin{aligned} V &= -y[A-B/(1-y)]/(1-y) \\ y &= -\exp(2\pi x/L) \\ A &= V_1 - V_2 \\ B &= (V_1^{1/2} + V_2^{1/2})^2 \\ L &= 2\pi(-2/F^*)^{1/2}(V_1^{-1/2} + V_2^{-1/2})^{-1} \end{aligned}$$

The potential has the limiting value of zero when $x \rightarrow -\infty$, goes through a single maximum of height V_1 as x increases, and has a limiting value of $V_1 - V_2$ as $x \rightarrow +\infty$. F^* is the second derivative of V at its maximum. The lower bound E_0 in the integral (1) is equal to zero when $V_1 \leq V_2$, and to $V_1 - V_2$ when $V_1 > V_2$. The three parameters used by Johnston and Heicklen are α_1, α_2, and u^*.

$$\begin{aligned} u^* &= h\nu^*/kT \\ \alpha_i &= 2\pi V_i/h\nu^*, \; i = 1,2 \\ \nu^* &= (1/2\pi)(-F^*/m)^{1/2} \end{aligned} \tag{2}$$

where m is an effective mass for tunneling (see ref. 2, p. 53). The integral (1) can be written in a symmetrical form by introducing a new variable, $\epsilon = (E - V_1)/kT$. It becomes

$$\Gamma^* = \int_{\epsilon_o}^{\infty} K e^{-\epsilon} d\epsilon \tag{3}$$

where $\epsilon_o = -v_1 = -V_1/kT$ when $V_1 \leq V_2$, and $\epsilon_o = -v_2 = -V_2/kT$ when $V_1 > V_2$. In terms of the parameters (2),

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the transmission probability K, derived by Eckart, has the form

$$K = [\cosh 2\pi(a_1 + a_2) - \cosh 2\pi(a_1 - a_2)] \times [\cosh 2\pi(a_1 + a_2) + D]^{-1}$$

$$\begin{aligned} 2\pi a_i &= \pi[(\epsilon + v_i)/c]^{1/2},\ i = 1,2 \\ c &= (1/8)\pi u^*(\alpha_1^{-1/2} + \alpha_2^{-1/2})^2 \\ D &= \cosh 2\pi d \text{ if } d \text{ is real} \\ &= \cos 2\pi|d| \text{ if } d \text{ is imaginary} \\ 2\pi d &= (4\alpha_1\alpha_2 - \pi^2)^{1/2} \end{aligned} \tag{4}$$

The method used to evaluate (3) is a modified 6-point Gaussian quadrature formula based on Legendre polynomials [4]. This was used even though the nature of the integral suggests using a formula based on Laguerre polynomials. When the number of evaluations of K is kept small, neither of these methods is satisfactory for the whole range of parameter values used by Johnston and Heicklen, so a variation of the first method was developed.

When ϵ gets large, K approaches unity. The method uses a Gaussian formula for that part of the integral where $K < 1$. The remainder where $K \approx 1$ is evaluated analytically. Thus, if $K(\epsilon) \approx 1$ for $\epsilon > \epsilon_b$, then

$$\int_{\epsilon_b}^{\infty} K(\epsilon)e^{-\epsilon}d\epsilon \approx \int_{\epsilon_b}^{\infty} e^{-\epsilon}d\epsilon = e^{-\epsilon_b}.$$

To evaluate ϵ_b, examine (4) as $\epsilon \to \infty$. One gets $\alpha_i \to \frac{1}{2}(\epsilon/c)^{1/2}$ and

$$K \to 1 - (1 + D)(\tfrac{1}{2}\exp(2\pi(\epsilon_b/c)^{1/2}) + D)^{-1} = K_b.$$

Setting K_b to some value close to unity and solving this equation for ϵ_b gives

$$\epsilon_b = c\left\{\frac{1}{2\pi}\log\left[\frac{2(1 + D)}{1 - K_b}\right]\right\}^2. \tag{5}$$

It happens that this value is not entirely satisfactory, and subtracting from it the average value of v_1 and v_2 gives better results. Also, in some cases, ϵ_b calculated in this way is very large. There is no point in using this value for ϵ_b as the upper bound of the Gaussian formula if the integrand at this point is negligible because of the exponential factor. Thus ϵ_b was kept below a certain fixed value ϵ_{max}. There resulted two parameters, K_b and ϵ_{max}, which were adjusted to minimize the sum of the squares of the differences between the results of this method and the corresponding tabulated values of Johnston and Heicklen.

3. Test of the method

Extensive testing of the accuracy of the method was performed by comparing it with an accurate 40-point Gaussian formula having the cutoff fixed at ϵ_b corresponding to $K_b = 0.999$ or at $\epsilon_b < 8$. In the ranges $0.5 \leq \alpha_1 \leq \alpha_2 \leq 20$, and $2 \leq u^* \leq 16$, a group of 10,910 comparisons was made. For this set there were the additional restrictions that when $\alpha_1 \geq 8$ then $u^* \leq 12$, or when $\alpha_1 \geq 16$ then $u^* \leq 10$. Note that $\Gamma^*(\alpha_1, \alpha_2) = \Gamma^*(\alpha_2, \alpha_1)$. A second set of 4,920 comparisons was made in the ranges $0.5 \leq \alpha_1 \leq \alpha_2 \leq 20$, and $0.05 \leq u^* \leq 1.5$. The results of these tests are given in table 1 in the form of histograms. These show the number of values which differ from the accurate values by a given percentage range. It can be seen from these results that very few values are in error by as much as 5 percent. Such accuracy should be quite adequate for most rate constant calculations.

TABLE I. *Tests of the accuracy of TUNL*

Variation from accurate values	Number of differences in percentage ranges	
Percent difference	Set I [a, b]	Set II [a, c]
−5.5%, −4.5%	3	1
−4.5, −3.5	4	5
−3.5, −2.5	6	19
−2.5, −1.5	30	26
−1.5, −0.5	3246	140
−0.5, 0.5	6811	4475
0.5, 1.5	343	227
1.5, 2.5	217	27
2.5, 3.5	170	
3.5, 4.5	78	
4.5, 5.5	2	
Standard deviations	0.77%	0.42%

[a] For both Sets I and II, $\alpha_2 \geq \alpha_1$. The values used were 0.5, 1.0, 1.5, 2.0, . . . 40.0.

[b] For Set I, $u^* = 2, 3, 4, \ldots 16$. Also if $\alpha_1 \geq 8$ then $u^* \leq 12$ and if $\alpha_1 \geq 16$ then $u^* \leq 10$.

[c] For Set II, $u^* = 0.05, 0.1, 0.2, 0.5, 1.0, 1.5$.

4. Appendix. Listing of TUNL

The parameters for this program are ALPH1 $= \alpha_1$, ALPH2 $= \alpha_2$, $U = u^*$, and $G = \Gamma^*$. It will calculate Γ^* accurately in the parameter ranges $0.5 \leq \alpha_1, \alpha_2 \leq 20$, and $0 < u^* \leq 16$ with the additional restrictions that when α_1 and $\alpha_2 \geq 8$ then $u^* \leq 12$, and when α_1 and $\alpha_2 \geq 16$ then $u^* \leq 10$.

```
      SUBROUTINE TUNL(ALPH1,ALPH2,U,G)
      DIMENSION X(6),W(6)
      DATA X/-.9324695,-.6612094,-.2386192,.2386192,.6612094,.9324695/
      DATA W/.1713245,.3607616,.4679139,.4679139,.3607616,.1713245/
      DATA PI,PI2,PISQ/3.1415926,6.2831853,9.8696044/
      COSH(Z)=.5*(EXP(Z)+EXP(-Z))
      UPI2=U/PI2
      C=.125*PI*U*(1./SQRT(ALPH1)+1./SQRT(ALPH2))**2
      V1=UPI2*ALPH1
      V2=UPI2*ALPH2
      D=4.*ALPH1*ALPH2-PISQ
      IF(D.LT.0) GOTO 10
      DF=COSH(SQRT(D))
      GOTO 11
   10 DF=COS(SQRT(-D))
   11 IF(V2.GE.V1) EZ=-V1
      IF(V1.GT.V2) EZ=-V2
      EB=AMIN1(C*(ALOG(2.*(1.+DF)/.014)/PI2)**2-.5*(V1+V2),3.2)
      EM=.5*(EB-EZ)
      EP=.5*(EB+EZ)
      G=0
      DO 20 N=1,6
      E=EM*X(N)+EP
      A1=PI*SQRT((E+V1)/C)
      A2=PI*SQRT((E+V2)/C)
      FP=COSH(A1+A2)
      FM=COSH(A1-A2)
   20 G=G+W(N)*EXP(-E)*(FP-FM)/(FP+DF)
      G=EM*G+EXP(-EB)
      RETURN
      END
```

5. References

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Generator Columns and High Pressure Liquid Chromatography for Determining Aqueous Solubilities and Octanol-Water Partition Coefficients of Hydrophobic Substances

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Generator columns packed with a solid support and loaded with a liquid organic phase make it possible to rapidly and conveniently equilibrate water with the organic phase. By coupling the generator column to an extractor column for high pressure liquid chromatographic analysis of the aqueous solution, errors from surface adsorption and loss to the atmosphere are avoided. Using this method, the mean values and confidence limits at a 95 percent confidence level of the aqueous solubility, S, and the octanol-water partition coefficient, P, of n-propylbenzene at 25 °C were found to be $S = (4.32 \pm 0.02) \times 10^{-4} M$ and $\log P = 3.720 \pm 0.003$.

Key words: generator column; hydrophobic; octanol; partition coefficient; propylbenzene; solubility; solute; water.

1. Introduction

Measurements of the aqueous solubilities of hydrophobic organic substances are important for understanding hydrophobic interactions in water [1, 2][1] and for predicting the distribution of pollutants in aquatic environments [3]. In the case of organic liquids, solubilities are often determined by a "shake-flask" method in which one shakes the liquid with water, allows the two phases to separate, and measures the concentration of the organic substance in the aqueous phase by an appropriate analytical technique.

A closely related type of measurement is the partition coefficient of a hydrophobic substance, describing its equilibrium distribution between immiscible organic and aqueous phases. Octanol-water partition coefficients have been used to predict the extent of bioconcentration of organic pollutants in trout muscle [4], and for making other chemical and biological correlations [5]. Partition coefficients are usually determined by the shake-flask method.

In any shake-flask experiment with a hydrophobic substance, the solute concentration in the aqueous phase is low. Consequently the measurement of this concentration can be seriously affected by the presence of colloidal dispersions (emulsions), adsorption of the solute onto surfaces of transfer vessels, and loss of a volatile solute into the atmosphere. These errors can be reduced, but only at a cost of inconvenience and increased time, by centrifuging or replacing the shaking by gentle stirring; prerinsing the glassware with the aqueous phase; and avoiding exposure of the aqueous phase to the atmosphere. A rapid, convenient method for preparing equilibrated aqueous phases without significant errors from such effects would be desirable.

For this purpose we have adapted the generator column method described by May *et al* [6]. A generator column has a solid support coated with a solid or liquid stationary phase. When water is pumped through the column, an aqueous solution is generated which is equilibrated with the stationary phase. May *et al* [6, 7] used their generator columns, packed with glass beads, mainly to measure solubilities of solid polycyclic aromatic hydrocarbons; the only liquid stationary phase used by them was benzene [7]. We have redesigned the generator column, changed the support to silanized silica in order to increase the coverage, and extended the stationary phase to hydrocarbon-octanol mixtures.

In this paper we describe the use of generator columns containing either propylbenzene (a liquid) for measuring the aqueous solubility, or a dilute solution of propylbenzene in octanol for measuring the octanol-water partition coefficient. For validation of the method, we also obtained data

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[1] Figures in brackets indicate literature references at the end of this paper.

using the more conventional stir-flask method. Propylbenzene concentrations were measured by high pressure liquid chromatography (HPLC) on a reverse phase analytical column with ultraviolet detection. The octanol phase was introduced into the chromatograph with a loop injector. For analysis of the aqueous phase, the solute was extracted onto an extractor column and eluted onto the analytical column by the HPLC mobile phase. The combination of a generator column, extractor column, and HPLC analysis is the same as the "dynamic coupled column liquid chromatographic" technique described by May *et al*[6].

2. Experimental section

2.1 Reagents

The n-propylbenzene (99.9%) and n-nonylbenzene (99%) were obtained from Chemical Samples Co.,[2] Columbus, Ohio. The n-octanol (Fisher Scientific Co., Certified grade) was washed successively with 0.1 M H_2SO_4, 0.1 M NaOH, and distilled water; it was then dried with $CaCl_2$, filtered and distilled at atmospheric pressure. HPLC grade methanol and water (Baker) were used to prepare the mobile phases for liquid chromatography. Ordinary distilled water was used for other aqueous solutions.

2.2 Generator Columns

The design of a typical generator column is shown in figure 1. The column consists of a 6 mm (outside diameter) Pyrex tube joined to a short enlarged section of 9 mm Pyrex tubing. To pack the column a plug of silanized glass wool was inserted at one end of the 6 mm tube. A silanized diatomaceous silica support (about 0.5 g of 100-120 mesh Chromosorb W, high performance grade, cleaned by Soxhlet extraction with ethanol and dried) was poured into the tube with tapping and retained with a second plug of silanized glass wool.

The column was loaded by pulling the liquid organic phase, propylbenzene or a propylbenzene-octanol mixture, through the dry support with gentle suction. Each propylbenzene-octanol mixture had previously been equilibrated with water using gentle stirring for several hours, and a portion of the equilibrated mixture was analyzed by HPLC.

After it was loaded, the column was set up vertically with its inlet end at the bottom and a Teflon outlet tube attached to the top. Water was pumped into the inlet from a Milton Roy Minipump. The water flow pushed a plug of the organic phase off the support and out the outlet tube. A new outlet tube consisting of clean $^1/_{16}$ in (1.6 mm) stainless steel tubing was then attached to the column with a clean ¼ in (6 mm) stainless steel column end fitting containing a 5-μm frit to protect the switching valve of the HPLC system (see sec. 2.4). During the generation of the aqueous solution, the column was inverted from its previous position to put the inlet at the top with the water flowing downward through the support, as shown in figure 1. The purpose of the section of larger diameter tubing below the support was to trap any of the lighter density organic phase that was pushed off the support by the water flow, in order to prevent droplets of this phase from being swept into the outlet tube.

Columns were reused by pumping methanol through to remove the organic phase, drying the support with a warm stream of nitrogen, and loading with a new organic phase.

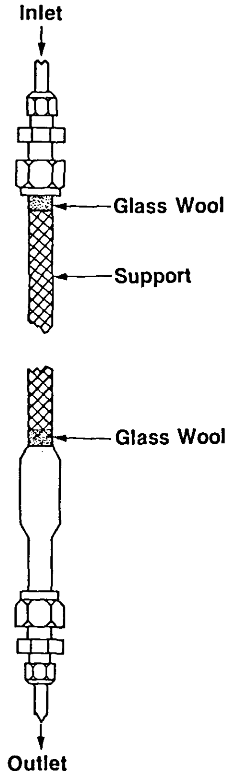

FIGURE 1. Generator column. The column is constructed from 6 mm and 9 mm Pyrex tubing. The length of the support is typically 12 cm. Connections to inlet and outlet tubing are by means of ¼ in (6 mm) stainless steel fittings with Teflon ferrules.

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[2] Certain trade names and company products are identified in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the products are necessarily the best available for the purpose.

2.3 Stir-flask equilibrations

For each equilibration, about 100 mL of water and about 4 mL of the organic phase were placed in a closed Pyrex vessel and stirred with a small glass-encased magnetic stirring bar. To prevent emulsion formation in the aqueous phase, vigorous stirring was avoided. Most of the organic layer was confined to a narrow neck at the top of the vessel. Above the neck was a $^{3}/_{8}$ in (9.5 mm) tube septum fittting for sampling of the organic layer after equilibration. The equilibrated aqueous phase was transferred to the HPLC system, with the aid of nitrogen pressure, through $^{1}/_{16}$ in (1.6 mm) stainless steel tubing attached to a ¼ in (6 mm) outlet tube.

2.4 HPLC System

The HPLC analytical system is shown schematically in figure 2. Two reciprocating piston pumps delivered the mobile phase (water or a methanol-water mixture) through two 6-port high pressure rotary valves and a 30 × 0.6 cm C-18 analytical column to an ultraviolet absorption detector operating at 254 nm. Chromatogram peaks were recorded and integrated with a recording integrator.

One of the 6-port valves was a sample injection valve used for injecting samples of either the octanol phase for analysis, or standard solutions of the solute in methanol for determining response factors. The sample loop volume was determined by a spectrophotometric method using basic chromate solutions which are known to be suitable as absorption standards [8]. The method consisted of measuring the absorbance at 373 nm of three loopfuls of an aqueous stock solution of K_2CrO_4 (1.3% by weight) diluted to 50 mL with 0.2 percent KOH, and measuring the absorbance of the same stock solution after diluting 1:500 with 0.2 percent KOH. From these absorbances the loop volume was calculated to be $(35.7 \pm 0.1)\,\mu$L.

The other 6-port valve in the system served as a switching valve for the extractor column which was used to remove solute from the aqueous solutions. The extractor column was a 6.6 × 0.6 cm stainless steel tube with stainless steel end fittings containing 5-μm frits, filled with a superficially porous reverse phase packing (Bondapak C_{18}/Corasil, Waters Associates). Aqueous solution from a stir-flask vessel or a generator column entered the switching valve through the $^{1}/_{16}$ in (1.6 mm) stainless steel tubing labelled "A" in figure 2. A water bath was used to thermostat to ± 0.05 °C the generator column (when used), the switching valve, the extractor column, and the interconnecting stainless steel tubing.

The procedure for analyzing the aqueous phase was first to flow the aqueous solution to waste with the switching valve in the inject position in order to equilibrate internal surfaces with the solution, thus insuring that the analyzed sample would not be depleted by solute adsorption on surfaces upstream from the valve. At the same time, water was pumped from the HPLC pumps in order to displace methanol from the extractor column. The switching valve was next changed to the load position to divert a sample of the solution through the extractor column, and the liquid leaving this column was collected in a weighing bottle. During this extraction step, the mobile phase was changed to a methanol-water mixture (generally 65% methanol pumped at 3 mL/min for propylbenzene analysis) to condition the analytical column. After the desired volume of sample had been extracted, the switching valve was returned to the inject position for elution and analysis. Provided that there was no breakthrough of solute from the extractor column during the extraction step, the chromatographic peak represented all of the solute in the sample. The solute concentration in the aqueous phase was calculated from the peak area and the weight of the extracted liquid collected in the weighing bottle.

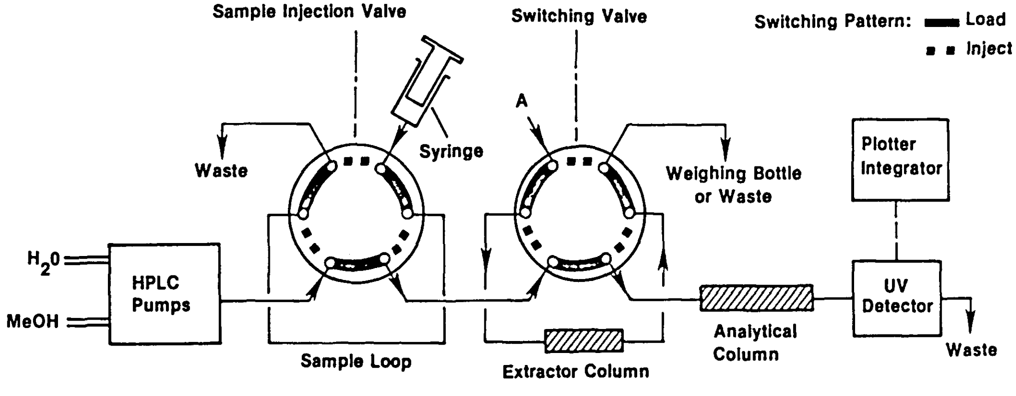

FIGURE 2. HPLC system. Connections shown by thin solid lines are $^{1}/_{16}$ in (1.6 mm) stainless steel tubing. Connection A is attached to the outlet of either a stir-flask vessel or a generator column.

3. Results and Discussion

3.1 Solubility

Table I lists our solubility results for propylbenzene. The aqueous samples were 2–6 mL in volume. The stir-flask and generator column results for comparable temperatures agree within experimental uncertainty. Our value at 25 °C, 4.3×10^{-4} M, is similar to the values for this temperature reported by Andrews and Keefer [9] (4.6×10^{-4} M) and by Hermann [1] (5.0×10^{-4} M). The temperature dependence of the solubility suggests that there is a minimum in the neighborhood of 20 °C. Solubility minima near 18 °C have been observed for benzene and its methyl, dimethyl, and ethyl derivatives [10]. In the case of propylbenzene, Gill *et al* [11] predict from the temperature dependence of the heat of solution that there is a solubility minimum at (18.6 ± 0.2) °C which is consistent with our results.

TABLE I. *Aqueous solubility of n-propylbenzene.*

t/°C^a	n^b	$c_w/10^{-4}$ M^c
stir-flask, stirred 16 h		
ambient	4	4.27 ± 0.06
generator column		
15.0	3	4.26 ± 0.05
20.0	2	4.25 ± 0.12
25.0	3	4.32 ± 0.02
30.0	3	4.45 ± 0.05

^{a} Equilibration temperature. Ambient is (23 ± 1) °C.

^{b} Number of aqueous solution samples analyzed.

^{c} Aqueous concentration; the mean value and the confidence limits at a 95 percent confidence level are listed.

3.2 Partition coefficient

The octanol-water partition coefficient, P, was calculated from the measured propylbenzene concentrations in the equilibrated octanol and aqueous phases by dividing the concentration in the octanol phase by the concentration in the aqueous phase.

The volumes of the aqueous phase samples used to obtain the partition coefficient values listed in table II were in the range 1–4 mL for the stir-flask results and 10–24 mL for the generator column results. The water flow rate through the generator columns was 2 mL/min. Further experiments with a generator column at 25 °C showed that within experimental uncertainty (standard deviation 3% or less) the measured aqueous concentration was independent of the water flow rate (in the range 0.5–2 mL/min) and was independent of the volume of sample passed through the extractor column (in the range 2–24 mL). These experiments show that under our experimental conditions the equilibration was complete in the generator column, and that there was no significant breakthrough of propylbenzene from the extractor column.

TABLE II. *Octanol-water partition coefficient of n-propylbenzene.*

c_{oct}/M^a	t/°C^b	n_{oct}^c	n_w^d	log P^e	uncertainty of log P^f
stir-flask, stirred 24 h					
0.222	ambient	4	4	3.734	0.016
stir-flask, stirred 41 h					
0.223	ambient	4	3	3.718	0.009
stir-flask, stirred 44 h					
0.220	ambient	3	4	3.711	0.007
generator column					
0.038	25.0	4	9	3.691	0.007
0.086	25.0	4	4	3.702	0.005
0.223	10.0	4	2	3.705	0.005
0.223	15.0	4	2	3.717	0.004
0.223	20.0	4	2	3.735	0.004
0.223	25.0	4	6	3.720	0.003
0.223	30.0	4	4	3.714	0.002
0.223	35.0	4	3	3.682	0.013

^{a} Concentration in octanol phase.

^{b} Equilibration temperature. Ambient is (23 ± 1) °C.

^{c} Number of octanol phase samples analyzed.

^{d} Number of aqueous solution samples analyzed.

^{e} Log P is calculated from log $(\bar{c}_{oct}/\bar{c}_w)$, where $\bar{c}_{oct}$ and $\bar{c}_w$ are the average values of the concentrations in the octanol and water phases.

^{f} Two times the calculated standard deviation (standard error) of log P.

Three stir-flask equilibrations with different stirring times were carried out (table II). With increased stirring time, there was a decrease in the partition coefficient values of about the same size as the experimental uncertainty. There is good agreement between these values and the generator column results.

The partition coefficient is seen to vary with temperature (table II), having a maximum in the vicinity of 20 °C. It is interesting to note that while the solubility and the partition coefficient of propylbenzene both vary with temperature, their product over the temperature range in which both quantities were measured (15–30 °C) is essentially constant (2.26 ± 0.05 M). This suggests that the heat of solution of propylbenzene in octanol is small.

The partition coefficient measurements at 25 °C (table II) show a small but systematic decrease of log P with decreasing concentration in the octanol phase. Extrapolation to infinite dilution gives log $P = 3.688 \pm 0.006$ at 25 °C. Iwasa *et al* [12] report log $P = 3.68 \pm 0.01$ from shake-flask measurements at ambient temperature, in excellent agreement with our results.

3.3 Colloidal dispersions from generator-columns

A potentially serious source of systematic error in any determination of the partition coefficient of a hydrophobic solute is the possible formation of colloidal droplets of the organic phase in the aqueous phase due to shear forces during the equilibration. Solute contained in these droplets would tend to make the apparent solute concentration in the aqueous phase higher than the concentration of the solute present in true aqueous solution. The calculated apparent partition coefficient would then be too low.

One may test for this source of error in a generator column by measuring the apparent partition coefficient of a solute which has a much higher partition coefficient than the solute of interest. We carried out such a test with a generator column loaded with a 0.08 M solution of nonylbenzene in octanol. A 25-mL sample of the aqueous phase from this column gave a chromatogram peak, barely visible above baseline noise, which represented an aqueous phase concentration of at most 1×10^{-7} times the octanol phase concentration. The largest volume fraction of the bulk octanol phase which could have been present as droplets in the aqueous phase, then, was 1×10^{-7}. If a 1×10^{-7} volume fraction of octanol phase had also been present in the propylbenzene partition coefficient measurements, the error in the apparent partition coefficient of propylbenzene would have been only 0.05 percent.

The value one would expect for the true partition coefficient of nonylbenzene, based on a linear extrapolation of log P versus carbon number from data [13] for the homologous series ethyl, n-propyl-, and n-butylbenzene is approximately 1×10^{7}. Thus the volume fraction of octanol in the aqueous phase must have been even less than 1×10^{-7}. We concluded that any error from colloidal dispersions in our determination of the partition coefficient of propylbenzene by the generator column method is much less than the uncertainty from random experimental errors.

3.4 Stripping of the stationary phase from generator columns

Because the organic stationary phase of a generator column is soluble to some extent in the water passing through the column, there is a continuous removal of the stationary phase. It can be shown from chromatographic theory that the composition of the generated aqueous solution should remain constant until the arrival at the downstream end of the support of a zone in which the stationary phase, or a component of this phase, has been completely stripped. At this point the generator column can no longer be used.

The volume of water required to strip the generator column used to measure the solubility of propylbenzene was much greater (on the order of 10 L) than the total volume of water passed through the column. In the case of a generator column used to determine a partition coefficient, it is the component of the organic phase having the smallest partition coefficient between the organic phase and the water phase which is stripped first. For propylbenzene-octanol mixtures, this component is octanol for which [14] log P = 3.15. We observed constancy in the propylbenzene concentrations of the aqueous solutions generated by columns loaded with these mixtures, as expected, until about one liter of solution had been generated; then a sudden increase in the concentration occurred. We attribute this increase to the stripping of the last amount of octanol and the saturation of the water with the liquid propylbenzene which remained on the support. The change was obvious and the measurements were discontinued as soon as it occurred.

3.5 Advantages of generator columns

Generator columns have several advantages over shake-flask and stir-flask methods for equilibrating water with a liquid organic phase. The flow rate of water through the column can be made slow enough to avoid colloidal dispersions, while the large interfacial area between the organic and aqueous phases allows rapid equilibration. When the column is part of a continuous and closed flow system, the system walls become equilibrated with the aqueous solution and errors from adsorption are avoided; also there is no exposure of the solution to the atmosphere. Only about 1 mL of the organic phase is sufficient to load the column, and the column will generate samples of the aqueous solution of whatever volume is needed for analysis until the organic phase has been stripped. Once a column has been loaded with a given organic phase, it is a simple matter to vary other parameters such as the temperature or the concentration of an added salt in the aqueous phase.

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Enthalpies of Solution of the Nucleic Acid Bases. 6. Guanine in Aqueous HCl and NaOH, and Guanine Hydrochlorides in Aqueous HCl

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The following values of the enthalphy of solution of well-characterized samples of guanine were obtained from measurements in an adiabatic solution calorimeter:

Solvent		$\Delta H(\infty, 298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
HCl(aq)	1st protonation	30.181 ± 0.032	814 ± 75 (at < 0.2 mol $\text{HCl}\cdot\text{L}^{-1}$)
			98 ± 8 (0.3 to 3.5 mol $\text{HCl}\cdot\text{L}^{-1}$)
	2nd protonation	34.98 ± 0.74	160 ± 15 (4.5 to 6.1 mol $\text{HCl}\cdot\text{L}^{-1}$)
NaOH(aq)		13.545 ± 0.034	156 ± 8 (0.1 mol $\text{NaOH}\cdot\text{L}^{-1}$)
H_2O (calculated)		27.2 ± 2.1	

The following enthalpies of protonation were calculated for guanine:

	$\Delta H(\infty, 298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1}$
Addition of 1 proton	3.0 ± 2.1
Addition of 2 protons	7.8 ± 2.2

Key words: Calorimetry; ΔC_p of reaction; $C_5H_5N_5O$; density; enthalpy of solution; $\text{Gua}\cdot\text{HCl}\cdot 1\ H_2O$; $\text{Gua}\cdot\text{HCl}\cdot 2\ H_2O$; $\text{Gua}\cdot 2\ \text{HCl}$; guanine (Gua); guanine hydrochlorides; heat capacity; nucleic acid base; solution calorimetry; thermochemistry.

1. Introduction

This is the final paper in this series [1-5].[1] It reports results from an incomplete study of the enthalpies of solution of guanine (Gua) and guanine hydrochlorides ($\text{Gua}\cdot n\text{HCl}$) in aqueous solutions of hydrochloric acid and of sodium hydroxide. Although there are still assumptions and unanswered questions, the results that were obtained are being published because the calorimetry is of high accuracy and considerable information is given characterizing the samples used.

It was impossible to measure the enthalpy of solution of guanine in water directly because of its low solubility (0.04 $\text{g}\cdot\text{L}^{-1}$ at 313 K [6]); however, a value at infinite dilution has been calculated. Enthalpies of solution of guanine in HCl solutions of various concentrations from 0.01 to 6.1 $\text{mol}\cdot\text{L}^{-1}$, and in NaOH solutions from 0.09 to 3.1 $\text{mol}\cdot\text{L}^{-1}$ were measured. Values for the ΔC_p of reaction were also determined. Enthalpies of solution of anhydrous guanine hydrochlorides in aqueous HCl solutions (0.3 to 6.0 $\text{mol}\cdot\text{L}^{-1}$) were measured. Enthalpies at infinite dilution of protonation and of proton dissociation were calculated for guanine and compared with analogous values obtained for adenine [1,5], another purine base. The exact sites of the ionizations are somewhat uncertain.

2. The Samples

Calorimetric measurements are reported here for the enthalpies of solution of four guanine samples as received

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[1] Figures in brackets indicate literature references at the end of this paper.

from commercial sources[2] and one sample obtained from solution, precipitation, and recrystallization of one of the commercial products; and for one sample of guanine hydrochloride, and three samples derived from it by recrystallization. The following information about the samples from commercial sources was obtained from labels, catalogs, and brochures:

Gua 1. A 25-g, Grade A sample purchased about 1970 from Calbiochem, Cat. No. 3700, Lot 73219. Analysis: Nitrogen, 46.32 percent (dry basis); Moisture, 0.4 percent, Chromat. Homogeneous. Spectra at pH 2: 250/260, 1.37; 280/260, 0.84; λ_{max}, 273 mμ; ε_{max}, 7330 (dry basis); λ_{min}, 267 mμ; ε_{min} 7200 (dry basis); $\lambda_{max\ 2}$ 248 mμ; $\varepsilon_{max\ 2}$ 11100 (dry basis).

Gua 2. Five 10-g samples obtained in November 1973 from Boehringer-Mannheim Corp. (made in Germany), Cat. No. 15516 NGAG, Kontrol-Nr. 7313507/ 1. Sept. 1975. Typical Analysis: Guanine (enzymatic) 98 percent, chromatographically pure. Stability: Store at room temperature; no detectable decomposition within 12 months.

Gua 3. A 5-g sample of guanine (2-aminohypoxanthine) for biochemistry from EM Labs. obtained in February 1974, Cat. No. 4221, Lot No. 2958531.

Gua 4. Four 25-g samples obtained in June 1974 from Calbiochem. Same as Gua 1 except Lot No. 400147.

Gua·HCl 1. A 25-g sample of the dihydrate obtained in February 1974 from Eastman Organic Chemicals, Cat. No. 1606, for chemical purposes, not for drug use. (This material had a pale yellow color.)

The following samples were derived from the commercial products by the methods described which are somewhat similar to those used by Stiehler and Huffman [7].

Gua 4b. Approximately 25 g of Gua 4 was dissolved in ~ 1 L of a boiling solution containing 5 percent (by volume) of concentrated HCl. The resulting solution was cloudy and amber colored. To remove the color, several grams of activated cocoanut charcoal were added to the boiling solution. The hot solution was filtered in a polypropylene Buchner-type funnel with Whatman No. 50 above No. 1 filter paper and a layer of filter paper pulp on the top. The filtrate was clear, but still amber colored. To precipitate the free guanine, hot concentrated ammonium hydroxide was added dropwise to the boiling solution until pH 3 to 5 was reached using indicating paper. The precipitate was collected on Whatman No. 50 above No. 1 filter paper, and washed with hot water. The filtrate was clear and colorless. The product was again dissolved, reprecipitated, filtered, and washed with hot water until the washings gave no test for Cl^- with $AgNO_3$ solution. This product was dried under vaccum over $Mg(ClO_4)_2$ for about one week.

Gua·HCl 2a, 2b, 2c, and 2d. A 25-g portion of Gua 4 was dissolved, filtered, reprecipitated, filtered again, and washed with hot water as described above for Gua 4b. This product was again dissolved in the 5 percent (~ 0.6 mol·L^{-1}) HCl solution and filtered. The filtrate (0.6 L) containing the Gua·HCl was allowed to cool overnight. A large volume of needlelike crystals formed and were separated from the saturated liquid by filtration. These crystals were dissolved slowly in a boiling solution containing 1.5 percent (by volume) of concentrated HCl. It was surprising that the crystals formed upon cooling this solution appeared to be of mixed composition—there were some yellowish plates or flakes mixed with small needles. The mixture was heated again; the boiling solution was cloudy and charcoal was added before filtering. The filtrate was clear and colorless. The free guanine was again precipitated, filtered, and washed. It was then dissolved in the hot 5 percent HCl solution. Again upon cooling, the abundance of needlelike crystals formed. About half (10 g) of these crystals were designated Gua·HCl 2a. The other half was redissolved in the 1.5 percent (~ 0.2 mol·L^{-1}) HCl solution, which, after cooling slowly, formed flaky crystals; this was designated Gua·HCl 2b. Both of these samples were dried for three days under vacuum in a desiccator containing $Mg(ClO_4)_2$. Gua·HCl 2a was resilient and did not break when tamped with a glass rod, but Gua·HCl 2b was brittle and the tamping produced a fine powder. Both of these samples were further dried for three days in a vacuum oven at ~ 340 K. Half of the samples, 2a and 2b, were heated at 370 K in a vacuum oven for four days and designated 2c and 2d, respectively.

The characterization and analyses of these materials will be discussed in the following subsections.

2.1. Volatile Matter and Hygroscopicity

The volatile matter (presumably H_2O) was determined from the loss in mass on heating in a vacuum oven where the samples were guarded by a liquid nitrogen trap from contamination by the oil vapors from the vacuum pump (the pressure was 1 kPa or less). The materials were heated at relatively low temperatures to reduce the possibility of decomposition. In table 1 the results of volatile matter determinations on samples of guanine and guanine hydrochlorides are given. Gua 1, 2, 3, 4, and Gua·HCl 1 are the commercial materials as received. Gua 4b was reprecipitated from Gua 4. Gua·HCl 2a and 2c were recrystallized from 5 percent (~ 0.6 mol·L^{-1}) HCl solution; Gua 2b and 2d were recrystallized from 1.5 percent (~ 0.2 mol·L^{-1}) HCl solution.

The samples heated at 340 K for 16 h or less, as listed in table 1, were spread out in flat aluminum dishes with tight fitting covers which were removed during heating. These samples were weighed after heating four h, then weighed again after each additional 2-h heating period. All other samples heated for longer periods were contained in glass weighing bottles or dishes.

Gua 2 differed from the other guanine samples in that there was a constant rate of loss in mass after the initial 4-h heating period. This was probably due to slow vaporization of some impurity. The other guanine samples were at constant mass after heating ~ 6 h at 340 K.

One of the two samples of Gua 1 dried at 370 K (table 1) had been previously dried at 340 K and subsequently exposed to air under the controlled conditions in this laboratory (relative humidity, $RH = 35 \pm 10$ percent, room temperature, $T = 296 \pm 1$ K). The essentially equal loss in mass for the two samples on drying at 370 K suggests that the

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[2] Commercial sources are named in this paper only for specific identification. The information presented is in no way intended as an endorsement or a condemnation by the National Bureau of Standards of any of the materials or services.

Table 1. Determination of volatile matter (or H_2O) in various samples of guanine and guanine hydrochlorides

Sample		Heating		[a]Mass
Designation	Mass	Time	Temperature	Lost
	g	h	K	%
Gua 1	2.20518	12	340	0.77 (0.75)
	3.10806	12	340	.77 (0.75)
	4.02280	12	340	.78 (0.75)
	1.53844	48	370	.96
	2.22628	48	370	[b] 1.01
Gua 2	1.98750	12	340	[c] 1.45 (1.41)
	2.01022	12	340	[c] 1.47 (1.42)
	2.06132	12	340	[c] 1.46 (1.42)
Gua 3	1.01588	12	340	1.52 (1.41)
	1.09410	12	340	1.48 (1.36)
	1.04799	12	340	1.49 (1.38)
Gua 4	3.78185	48	370	1.70
Gua 4b	3.33798	48	370	0.84
[d]Gua•HCl 1	2.24860	10	340	[e] 8.80 (8.4)
	2.64132	16	340	[e] 8.85 (8.4)
	3.03390	12	340	[e] 8.84 (8.4)
	17.550	70	340	14.2
Gua•HCl 2a	6.590	70	340	0.76
Gua•HCl 2b	5.895	70	340	0.59
[f]Gua•HCl 2c	3.205	95	370	< 0.03
[g]Gua•HCl 2d	2.240	95	370	0.36

[a] Values given are for the total heating time, those in parentheses are for the mass lost after heating 4 h.

[b] This sample was previously dried at 340 K and subsequently exposed to air (T = 296 K, RH = 35 %).

[c] After the initial 4-h heating period, this material lost mass at the constant rate of 0.1 $mg \cdot h^{-1}$ for an additional 8 h. The other guanine samples were at constant mass after heating a total of 6 h.

[d] This material was nominally the dihydrate which was confirmed by density measurements. Theoretical H_2O = 16.1 %.

[e] An additional 0.5 % loss occurred after heating 24 h at 370 K (total loss = 9.3 %; removal of 1 H_2O of hydration corresponds to a loss of 8.0 %).

[f] This was a portion of Gua•HCl 2a which had been dried at 340 K.

[g] This was a portion of Gua•HCl 2b which had been dried at 340 K.

moisture lost on drying at 340 K was reabsorbed upon exposure to air. Therefore, the calorimetric samples of guanine were transferred in the room air and corrected for the moisture found as volatile matter.

Two H_2O determinations on Gua 1 and 2 by Karl Fischer titrations (the method was previously described [1]) indicated 0.64 and 1.05 percent H_2O, respectively. These values are not considered to be as reliable as the volatile matter determinations for small amounts of H_2O, especially because the guanine was only slightly soluble in the methanol solvent.

The guanine hydrochloride, Gua·HCl 1, as received from the commercial source, was nominally the dihydrate. It was hygroscopic; a gain in mass of 0.1 percent was observed in a period of 5 min exposure to room air (*RH* = ∿ 35%). All subsequent operations transferring this material were performed in dry atmospheres. The first 3 samples of Gua·HCl 1 listed in table 1 were in Al dishes and lost a total of 9.3 percent H_2O (8.4% in the first 4 h at 340 K) which is greater than the theoretical loss for one hydration H_2O (8.0%). Another larger sample in a glass dish heated at 370 K for ∿ 70 h lost mass nearly equivalent to 2 H_2O. Thus it appears that the second water of hydration is removed relatively slowly upon heating at this temperature.

Gua·HCl 2a and 2b were products of recystallization of reprecipitated Gua 4 from HCl solutions (0.6 $mol \cdot L^{-1}$ and 0.2 $mol \cdot L^{-1}$, respectively). Both products were dried overnight at 296 K under vacuum in a desiccator containing $Mg(ClO_4)_2$. It appears that this removed most of the water of hydration, because vacuum drying at 340 K for 70 h resulted in a mass loss of less than 1 percent (see table 1). About half of these dried products were further dried 95 h at 370 K and are designated Gua·HCl 2c and 2d, respectively, in table 1.

Small portions of the guanine hydrochloride samples listed in table 1 as dried for 70 h or longer were transferred (in a glove box containing a desiccant) to weighing bottles for hygroscopicity observations. After an initial weighing, the caps to the bottles were removed and the samples were exposed to the room air while standing in the balance case. The weights were recorded at various intervals over a period of three days. The cumulative changes in mass for the 5 samples are shown in table 2. Gua·HCl 2a and 2c were not hygroscopic under these conditions, but Gua·HCl 2b and 2d absorbed moisture for several hours. The moisture absorbed was approximately equal to that lost on heating and

Table 2. Cumulative mass changes observed upon exposure of dried Gua•HCl samples to air (RH = ∿ 35 % and 296 K).

	Gua•HCl sample				
Δt	1	2a	2b	2c	2d
min			mg		
15	1.7	0.0	0.5	-0.1	0.4
85	7.5	.0	1.8	.0	1.5
205	6.3	.0	2.2	.0	1.8
1310	31.5	- .1	2.4	.0	2.0
2785	32.8	- .3	2.5	.0	2.1
4405(∿ 3 days)	33.4	- .6	2.4	- .2	2.0
Sample Mass, mg	559	340	284	211	221
Total Δ mass, %	6.0	-0.2	0.8	0.1	0.9

is apparently not water of hydration. Gua·HCl 1 (originally the dihydrate) was still absorbing moisture after 3 days and the 6 percent gain in mass was approaching the 8 percent equivalent of 1 H_2O.

All calorimetric samples of the guanine hydrochlorides were the dried material. Transfers to the sample holder were made in a dry atmosphere to prevent absorption of moisture by the samples.

2.2. Elemental Analysis of the Guanine Hydrochlorides

Portions of the guanine hydrochloride samples which had been heated under vacuum for 70 h or longer (see table 1) were transferred in a glovebox to glass vials with tight-fitting plastic caps for shipment to the analytical laboratory. Four days later, the microanalyses were performed; the results are given in table 3. The compositions of Gua·HCl 1 and 2c correspond to that of the anhydrous monohydrochloride, but that of Gua·HCl 2d is closer to the hemihydrochloride. This might be expected since the latter sample was recrystallized from a more dilute HCl solution than Gua·HCl 2c.

Although the compositions of Gua·HCl 1 and 2c (table 3) are similar, they must be of different structure because it was shown in section 2.1 that the Gua·HCl 1 was very hygroscopic and the Gua·HCl 2c was not. It is important that the dried guanine hydrochlorides are anhydrous. Only the dried materials were used in the calorimetric experiments. It will be assumed that samples 1 and 2c are the anhydrous monohydrochloride and that sample 2d is the anhydrous hemihydrochloride although these may be erroneous assumptions.

2.3. Density

The densities of several samples of guanine and the guanine hydrochlorides were measured by a displacement method in 25-cm³, Gay-Lussac-type pycnometers using Eastman ACS spectroscopic grade CCl_4 (density = 1.5898 $g \cdot cm^{-3}$ under the laboratory conditions; this is the mean of 3 measurements for which the average deviation was 0.0002 $g \cdot cm^{-3}$). Details of the method are described in the first paper of this series [1]. The results of these measurements are given in table 4.

After the density measurement for Gua 1, the sample was collected on filter paper, dried in air, and weighed; there was a loss in mass of ~ 1 mg or < 0.1 percent. When the filtrate was evaporated to dryness there was no visible residue. Thus, the solubility of guanine in CCl_4 was insignificant in the density determinations.

The results of density measurements given in table 4 for Gua 1, 3, 4, and Gua·HCl 1 were obtained on samples as received from commercial sources; the other measurements were made on the dried samples (see sec. 2.1). For calculating the buoyancy factor, 1.000546, used in this work to cor-

Table 3. Microanalysis[a] of 3 dried samples of the guanine hydrochlorides and theoretical compositions of some probable components.

Sample Designation	Empirical Formula	[b] Molar Mass	C	H	O	N (Kjeldahl)	Cl
		g/mol	per cent				
Gua·HCl 1			31.73	3.47	8.88	37.26	18.34
Gua·HCl 2c			31.82	3.04	8.60	36.61	18.72
Gua·HCl 2d			36.07	3.56	10.33	41.85	7.66
Theoretical Composition:							
Gua	$C_5H_5N_5O$	151.1274	39.74	3.33	10.59	46.34	0.00
Gua·1/2 HCl	$C_5H_{5.5}N_5OCl_{0.5}$	169.3578	35.46	3.27	9.45	41.35	10.47
Gua·1 HCl	$C_5H_6N_5OCl$	187.5883	32.01	3.22	8.53	37.33	18.90
Gua·2 HCl	$C_5H_7N_5OCl_2$	224.0492	26.80	3.15	7.14	31.26	31.65
Gua·HCl·1 H_2O	$C_5H_8N_5O_2Cl$	205.6035	29.21	3.15	15.56	34.06	17.24
Gua·HCl·2 H_2O	$C_5H_{10}N_5O_3Cl$	223.6187	26.86	4.51	21.46	31.32	15.85

[a] Analyses by Micro-Analysis, Inc., Wilmington, DE

[b] Obtained from 1975 Table of Atomic Weights [12].

Table 4. Densities of Gua and Gua·HCl samples measured by a displacement method.

Sample Designation	Mass	Density
	g	g/cm^3
Gua 1	1.3	1.725
Gua 3	1.3	[a,b] 1.727
Gua 4	0.8	1.702
Gua 4b	1.3	1.720
Gua·HCl 1	0.5 0.4	[a] 1.56 1.54
Gua·HCl 2a	0.3	1.64
Gua·HCl 2c	0.3 0.4	1.64 1.64
Gua·HCl 2d	0.2 0.3	[c] 1.53 [c] 1.50

[a] A few floating particles were observed.

[b] Sample appeared wet by CCl_4 with little degassing.

[c] Vigorous bubbling apparently from degassing.

rect the guanine weights to vacuum, the density of guanine, 1.72 $g \cdot cm^{-3}$ was taken from the results in table 4.

This method for determining densities proved unsatisfactory for the guanine hydrochlorides. The densities measured did not agree with the elemental analyses. It was suspected that impurities in the CCl_4 reacted with the dried samples to change their compositions during the density measurements.

It was reported in Beilsteins Handbuch [8] that the hydrogen chloride salt of guanine may crystallize as the monohydrate (molar mass = 205.60), as the dihydrate (molar mass = 223.62), or as guanine dihydrochloride (molar mass = 224.05). Broomhead [9] prepared two crystalline guanine hydrochloride samples. The first was found to have molar mass = 223, density = 1.562 $g \cdot cm^{-3}$, and microanalysis indicated that it was the monohydrochloride dihydrate rather than the dihydrochloride. The second sample had density = 1.662 $g \cdot cm^{-3}$ and molar mass = 205.2, and was apparently the monohydrate. (Details of the preparations and measurements were not given.)

Our density measurements confirmed that Gua·HCl 1 (as received) was the dihydrate (although the anhydrous material prepared from it was used in the calorimetric experiments). However, the measurements on the dried samples did not agree with the elemental analyses. Therefore, these density values were used only for calculating buoyancy factors for determining the mass of samples; the resulting errors are relatively small.

2.4. Other Analyses

The heat capacities at 298 K, C_p°, of two crystalline guanine samples were measured by Ernesto Friere using a drop microcalorimeter at the University of Virginia. He obtained 1.063 $J \cdot g^{-1} \cdot K^{-1}$ for Gua 1 and 1.079 $J \cdot g^{-1} \cdot K^{-1}$ for Gua 4b with an estimated uncertainty of 0.008 $J \cdot g^{-1} \cdot K^{-1}$ for the measurements [10].

Emission spectrochemical analyses[3] of samples of Gua 1, 2, 3, and 4 revealed no impurities in the samples greater than the limits of detection reported for adenine [1].

Analysis of gas chromatograms[4] obtained from trimethylsilylation of Gua 1, 2, 3, 4, and 4b led to the conclusion that Gua 1 and 3 appear to have somewhat less impurity than the others. No specific conclusions could be drawn from these measurements.

The following information was reported from analysis[5] of X-ray powder diffraction patterns. Gua 1, Gua 3, Gua 4, and Gua 4b all produced weak patterns which could be identified as crystalline guanine. No major impurities were found. Gua 3 produced the pattern with greatest detail. The three samples of guanine hydrochlorides, Gua·HCl 1, 2c, and 2d, were all crystalline. The pattern from Gua·HCl 1 was distinctly different from those of 2c and 2d, which were sufficiently similar to indicate that they had the same crystallographic lattice. It is not possible to draw conclusions about the states of hydration.

No impurities were identified or detected from analyses by paper and thin layer chromatography (TLC) in the samples of Gua 1, 2, 3, 4, and 4b. Details of the procedures and detection limits were described previously [1]. The spotting solutions contained ∼ 0.01 mol Gua/L of aqueous HCl or NaOH (1 $mol \cdot L^{-1}$). (Guanine was nearly insoluble in the hot NH_4OH used for the other bases). The R_f values (distance traveled by the major component/distance traveled by the solution) were determined for the 5 guanine samples using TLC plates coated with 250 nm of MN300 Cellulose(C), or (CF) which also contains a fluorescent indicator, and Whatman No. 1 and No. 40 chromatography papers, and 4 different carrier solutions described in table 5. The R_f values obtained for guanine samples are compared with those given by the National Academy of Sciences (NAS) [11] for similar solutions and procedures. The NAS values are lower than in

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[3] Analyses by J. A. Norris, Gas and Particulate Science Division, Center for Analytical Chemistry, National Measurement Laboratory.

[4] Analysis by D. Enagonio, Organic Analytical Research Division, Center for Analytical Chemistry, National Measurement Laboratory.

[5] Analysis by Camden R. Hubbard, Crystallography Section, Ceramic, Glass, and Solid State Science Division, National Measurement Laboratory.

Table 5. R_f values for 5 guanine samples using TLC plates and papers with 4 carrier solutions, A,B,C, and D[a].

Gua Sample	Solvent	A			B				C			D			
		[b]C	CF	P-40	C	CF	P-1	P-40	C	CF	P-40	C	CF	P-1	P-40
1	HCl(aq, 1 $mol \cdot L^{-1}$)	0.64	0.77	0.73	0.47	0.16	0.40	0.50	0.46	0.25	0.54	0.53	0.32	0.45	0.42
2		.66	.76	.76	.51	.16	.43	.50	.47	.25	.52	.57	.34	.43	.44
3		.67	.76	.76	.52	.16	.41	.48	.46	.25	.54	.57	.33	.44	.45
4		.69	.76	.74	.51	.18	.41	.48	.48	.25	.54	.56	.32	.45	.47
4b		.66	.75	.72	.51	.13	.43	.48	.46	.26	.56	.54	.32	.45	.47
NAS [11]				.66				.27			.47				.40
1	NaOH(aq, 1$mol \cdot L^{-1}$)	---	0.76	0.71	---	0.25	0.36	0.58	---	0.19	0.47	---	0.86	0.50	0.49
2		---	.73	.72	---	.26	.39	c	---	.18	.38	---	.83	.49	.50
3		---	.71	.73	---	.26	.34	c	---	.19	.36	---	.86	.47	.51
4		---	.74	.72	---	.25	.35	c	---	.18	.42	---	.85	.48	.50
4b		---	.73	---	---	.26	.36	c	---	.17	.41	---	.84	.48	.50

[a] The volume compositions of the carrier (or tank) solutions was as follows:

Soln A: 5 parts of iso-butyric acid + 3 parts of $NH_4OH(aq, 0.5\ mol \cdot L^{-1})$.

Soln B: 7 parts of iso-propyl alcohol + 1 part of conc. NH_4OH + 2 parts of H_2O.

Soln C: 7 parts of 95 % ethyl alcohol + 3 parts of sodium acetate (aq, 1 $mol \cdot L^{-1}$).

Soln D: H_2O adjusted to pH 10 with NH_4OH (∿ 1 drop of conc. NH_4OH in 300 mL H_2O).

[b] C is a glass TLC plate coated with 250 μm of MN300 cellulose.

CF is the same as C except it includes a fluorescent indicator.

P-1 and P-40 are Whatman No. 1 and No. 40 chromatography papers.

[c] Bands at R_f = ∿ 0.48 instead of spots.

this work, but are still within the uncertainties to be expected under differing experimental conditions. This was also true for the R_f values reported previously in this series [1-4].

3. Enthalpy of Solution Measurements

The relative molar masses used in this work were obtained from the 1975 Table of Atomic Weights [12]; the unit of energy is the joule as defined in the International System of Units (SI). Uncertainties are expressed as standard deviations except as otherwise noted. The weights in air for all crystalline samples and solutions have been corrected to vacuum (mass) as described previously [13]. For calculating buoyancy factors, densities for the aqueous HCl and NaOH solutions were obtained from the Handbook of Chemistry and Physics [14].

Enthalpy of solution measurements were made in a platinum-lined silver, adiabatic, vacuum-jacketed, solution calorimeter. The calorimeter, procedures used for measurements, electrical measuring instruments, and corrections to the experimental data have been described [13, 15].

The calorimetric measurements reported here were made intermittently between November 1973 and April 1975. The stirring rate was 700 revolutions per minute (rpm) for all experiments using Gua and Gua·HCl in HCl solutions (except Nos. 888, 889, and 891 at 450 rpm). The rate was 450 rpm for the measurements of Gua in NaOH solutions.

The following definitions apply to expressions in the text and in the tables:

Expt. No. is a serial number for experiments with this calorimeter and indicates the chronological order of the experiments.

Reaction period is the elapsed time between the initiation of the reaction and the beginning of the rating period which follows the reaction. Occasionally, there are long reaction periods which are probably the result of the way the sample holder opens. If the cylinder containing the sample does not tilt slightly, some of the sample may remain in it and dissolve very slowly. However, since heat leak corrections have been shown to be negligible in this calorimeter, the rate of the reaction does not seriously affect the results.

ϵ_i and ϵ_f are the electrical energy equivalents of the initial and final systems.

ΔT_{corr} is the observed temperature change corrected for constant energy sources such as stirring energy.

Q_{obs} is the observed heat of reaction;

$$Q_{obs} = \left(\frac{\epsilon_i + \epsilon_f}{2}\right) \Delta T_{corr}.$$

Q_v is the correction for vaporization of water into the air space contained in the sample holder;

$$-q_v = \Delta H_v \left(V - \frac{s}{d}\right) (1 - RH)$$

where ΔH_v is the enthalpy of vaporization of water /unit volume at the mean temperature of the reaction [16], V is the internal volume of the sample holder (in this work, 0.74 cm^3), s is the mass of sample, d is the density of the sample, and RH is the relative humidity of the atmosphere in which the sample was transferred to the sample holder ($RH = \sim 0.35$ for the room air or $RH = \sim 0$ in the glove box).

q_{diln} is a correction for dilution by the sample water of the HCl solutions. This correction was negligible (n) in the dilute HCl solutions (< 1 mol•L^{-1}) and in the NaOH solutions. Enthalpies of dilution for the more concentrated HCl solutions were taken from Parker's tabulation [17].

Q_r is the specific corrected heat of the reaction;

$$Q_r = (Q_{obs} - q_v - q_{diln})\, s^{-1}.$$

T_r is the mean temperature of the reaction.

Corr_{ST} is the correction to the standard or reference temperature, 298.15 K;

$$\mathrm{Corr}_{ST} = \Delta c_p\, (T_r - 298.15 \text{ K})$$

where the values for Δc_p, the change in specific heat capacity during the reaction, are determined in this work as

$$\Delta c_p = -\left(\frac{Q_{rT_1} - Q_{rT_2}}{T_2 - T_1}\right).$$

The values of Q_r are from 2 experiments at different temperatures, T_1 and T_2. The specific enthalpy of solution at the reference temperature is $-(Q_r - \mathrm{Corr}_{ST})$; the molar enthalpy of solution is

$$\Delta H(298.15 \text{ K}) = -(Q_r - \mathrm{Corr}_{ST})M$$

where M is the relative molar mass of the sample.

3.1. ΔH_{soln} of Gua in Aqueous HCl

Gua 1 was used for most of the measurements of the enthalpy of solution because it was white crystalline material which appeared to be relatively free of impurities and the volatile matter found was less than in the other three samples from commercial sources. It was assumed that the discoloration in Gua 3 was from impurity although none was detected or identified in the analytical work described in section 2. Gua 4 was also slightly discolored and was used in preparing other samples of guanine and guanine hydrochlorides by reprecipitation and recrystallization. A few measurements of the enthalpy of solution were made with samples other than Gua 1 for comparison.

In table 6 are the data from the measurements of the enthalpy of solution in HCl solutions of various concentrations; the arrangement of the experiments is in order of increasing HCl concentration. The mass of guanine was ∼ 0.2 g (1.2 to 1.5 mmol) and the volume of the solution was ∼ 300 cm^3 in all experiments. The experiments are divided into 3 groups because the measured values for the ΔC_p of the reaction were significantly different at different HCl concentrations.

Table 7 shows the Expt. Nos. (from table 6) for which values of Q_r and T_r were used in calculating Δc_p for the reaction at five concentrations of HCl. The Δc_p for group 1, 5.39 $J \cdot g^{-1} \cdot K^{-1}$, was derived from only one pair of experiments at the concentration, 0.1013 $mol \cdot L^{-1}$. It was applied in the calculation of Corr_{ST} for this entire group because a precipitate formed in the final solutions of all these experiments, but not in those of Groups 2 and 3. At first, this undissolved material was believed to be unreacted guanine. However, observation of a non-calorimetric experiment revealed the immediate formation of a voluminous white precipitate (presumably the hydrochlorides since there was an excess of Cl^- in even the most dilute solution), only part of which dissolved in the dilute solutions. The concentration where the dissolution of this precipitate was complete is shown graphically in figure 1 which is a plot of the values given in table 6 for ΔH(298.15 K) as a function of HCl concentration. The values for the enthalpy of solution increase sharply with increasing HCl concentration until a precipitate is no longer visible in the final solution, ∼ 0.2 $mol \cdot L^{-1}$.

The values measured for Δc_p of the reaction (table 7) at the HCl concentrations, 0.307 and 3.46 $mol \cdot L^{-1}$, agreed, and the mean value, 0.65 $J \cdot g^{-1} \cdot K^{-1}$, was used in calculating Corr_{ST} for the experiments in Group 2. At HCl concentrations, 5.45 and 6.09 $mol \cdot L^{-1}$, the values for Δc_p also agreed, and the mean value, 1.06 $J \cdot g^{-1} \cdot K^{-1}$, was used to obtain Corr_{ST} for experiments in Group 3. It was questionable whether the Δc_p value from Group 2 or 3 should be used for the 6 experiments using HCl solutions between the concentrations, 3.46 and 5.45 $mol \cdot L^{-1}$. The use of either value for Δc_p resulted in lower values for ΔH(298.15 K) than would correspond to the curve for Group 2 (see fig. 1). Therefore, it was assumed that the second protonation occurred at the HCl concentration of 4 $mol \cdot L^{-1}$ or less, and the 6 experiments in question were included in Group 3.

Table 6. Data from the measurements of the enthalpy of solution of guanine in aqueous HCl solutions.

Expt. No.	Gua No.	Gua Mass[a] g	HCl Soln. No.[b]	HCl Soln. Conc. mol/L	HCl Soln. Mass g	Reaction Period min	Electrical Energy Equivalent ε_i J/K	Electrical Energy Equivalent ε_f J/K	$-\Delta T_{corr}$ K	$-Q_{obs}$ J	$-q_v$ J	$-q_{diln}$ J	$-Q_r$[c] J/g	T_r k	$Corr_{ST}$ J/g	ΔH(298.15 K) J/g	ΔH(298.15 K) kJ/mol
Group 1:																	
982	1	0.20262	(54)	0.0101	302.82	12	1737.20	1736.98	0.001726	2.998	0.02	n	14.20	298.195	0.24	14.46	2.18
981	1	.19803	(54)	.0251	303.17	17	1737.57	1737.36	.004146	7.204	.02	n	36.28	298.188	0.20	36.08	5.45
980	1	.21185	(54)	.0507	302.50	67	1733.28	1732.83	.008982	15.566	.02	n	73.38	298.173	0.12	73.26	11.07
978	1	.22297	54	.1013	302.47	47	1728.67	1728.47	.015982	27.626	.02	n	123.81	298.173	0.12	123.69	18.69
979	1	.21837	54	.1013	302.48	52	1728.18	1727.93	.023053	39.837	.04	n	182.24	309.013	(used for ΔC_p value)		
983	1	.21740	50	.183	302.42	57	1721.85	1721.44	.023552	40.548	.02	n	186.42	298.173	0.12	186.30	28.16
Group 2:																	
977	1	0.21403	51	0.307	302.47	27	1712.42	1711.75	0.024258	41.532	0.02	n	193.95	298.139	-0.01	193.96	29.31
1028	1	.19891	51	.307	302.49	12	1713.17	1712.41	.023388	40.059	.04	n	201.19	308.996	7.05	194.14	29.34
1042	2	.20598	52	.312	307.44	32	1731.80	1731.19	.022700	39.305	.02	n	190,72	297.878	-0.18	190.90	28.85
1044	3	.20677	52	.312	307.46	122	1731.51	1730.99	.021935	37.975	.02	n	183.56	297.880	-0.18	183.74	27.77
984	1	.20260	55	.787	302.46	7	1676.00	1676.00	.022348	37.455	.02	n	184.85	298.233	0.05	184.80	27.93
1025	4b	.20188	55	.787	302.48	22	1676.09	1674.73	.021279	35.651	.02	---	176.50	298.118	-0.02	176.52	26.67
1026	4	.19267	55	.787	302.45	12	1675.32	1674.70	.020364	34.110	.02	n	176.93	298.222	0.05	176.88	26.73
976	1	.20089	56	.997	307.43	12	1680.61	1680.54	.021528	36.179	.02	n	180.13	298.106	-0.03	180.17	27.23
1024	4b	.19758	56	.997	307.47	22	1679.14	1678.53	.020356	34.174	.02	---	172.86	297.916	-0.15	173.01	26.15
1027	4	.19492	56	.997	307.48	27	1680.13	1679.16	.019276	32.380	.02	n	166.01	298.152	0.00	166.01	25.09
1036	1	.20387	(59)	3.46	307.95	37	1537.65	1537.48	.017645	37.130	.07	0.03	132.58	319.212	13.7	118.9	17.97
1037	1	.19450	(59)	3.46	308.00	97	1531.33	1530.54	.016095	24.640	.04	.03	126.33	309.242	7.20	119.12	18.00
Group 3:																	
1038	1	0.19831	(60)	4.49	307.87	32	1484.56	1484.76	0.013859	20.576	0.07	0.05	103.15	319.198	22.3	80.8	12.22
1039	1	.19818	60	5.01	307.44	17	1457.88	1458.00	.012060	17.583	.07	.09	87.91	319.201	22.3	65.6	9.92
1032	1	.19996	59	5.06	302.45	142	1421.17	1421.01	.009143	13.377	.02	.09	66.35	298.002	-0.16	66.51	10.05
1021	1	.19638	58	5.13	302.42	131	1417.64	1418.16	.008475	12.017	.02	.09	60.63	298.251	0.11	60.52	9.15
1022	4	.20424	58	5.13	302.46	22	1418.07	1418.40	.007594	10.770	.02	.09	52.19	298.119	-0.03	52.22	7.89
1023	4b	.20133	58	5.13	302.44	42	1417.09	1417.78	.008161	11.568	.02	---	57.36	297.443	-0.08	57.44	8.68
1040	1	.19648	(61)	5.45	313.46	112	1438.37	1438.54	.007112	10.230	.04	.11	51.40	298.109	-0.05	51.35	7.76
1041	1	.19875	(61)	5.45	313.42	22	1449.04	1448.76	.008864	12.843	.04	.11	63.86	309.116	11.6	52.24	7.90
1043	2	.19478	61	5.98	312.35	27	1422.42	1422.03	.005620	7.993	.04	.22	39.70	309.002	11.5	28.20	4.26
888	1	.18419	47	6.09	312.37	32	1407.85	1407.94	.004037	5.684	.02	.16	29.88	298.188	0.04	29.84	4.51
889	1	.19862	47	6.09	312.33	22	1407.51	1407.67	.004250	5.982	.02	.18	29.11	298.244	0.10	29.01	4.38
891	1	.19344	47	6.09	312.33	12	1417.77	1418.55	.005625	7.977	.04	.17	40.15	308.889	11.4	28.77	4.35

[a] Corrections to the mass of guanine for volatile matter (H_2O) reported in sec. 2.1 are as follows: Gua 1, 1.0 %, Gua 2 and 3, 1.5 %; and Gua 4, 1.7 %. No corrections were made to Gua 4b because the dried sample was used in the measurements.

[b] HCl Soln. No. is the number of the stock solution from which the calorimetric solution was taken. The numbers in parentheses indicate that the stock solution was diluted to obtain the calorimetric solution.

[c] $-Q_r$ includes corrections of - 0.027 J(No. 976) and - 0.014 J(No. 984) for brief departures of the shield temperature from that of the vessel because the reaction was fast.

[d] The measured values for ΔC_p at different HCl concentrations did not agree, therefore the following values were used for corrections to the reference temperature: 5.4 $J \cdot g^{-1} \cdot K^{-1}$ for Group 1; 0.65 $J \cdot g^{-1} \cdot K^{-1}$ for Group 2; and 1.06 $J \cdot g^{-1} \cdot K^{-1}$ for Group 3.

Table 7. Values of Δc_p for the reaction of Gua 1 in HCl solutions of various concentrations. (The uncertainties are estimated.)

Expt. Nos.	HCL conc.	Δc_p	Mean	Group
	mol/L	J/g·K	J/g·K	
978 and 979	0.1013	5.39 ± 0.50	---	1
977 and 1028	0.307	0.67	0.65 ± 0.05	2
1036 and 1037	3.46	0.63		
1040 and 1041	5.45	1.13	1.06 ± 0.10	3
891 and mean of 888 and 889	6.09	1.00		

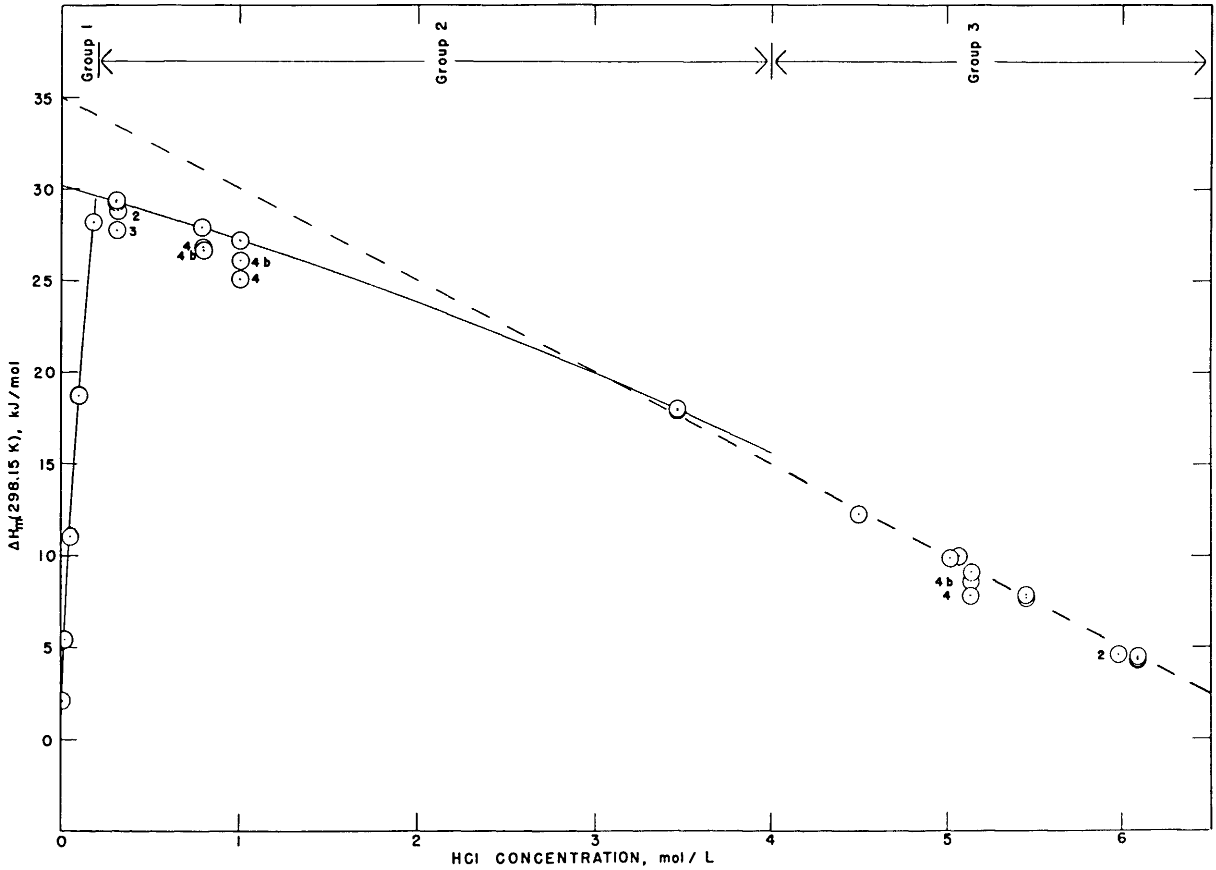


FIGURE 1. Plot of the values for the enthalpy of solution of guanine as a function of the concentration of the solvent, aqueous HCl. Group 1 shows the endothermic effect of dissolution of the guanine hydrochloride formed, Group 2 shows the exothermic effects of dilution, and the slope change in Group 3 probably indicates a protonation of the guanine molecule. Gua 1 was used for all experiments except those marked 2, 3, 4, and 4b which used other guanine samples for comparison. (see text).

Further justification for this grouping was provided by the differences in the electrical energy equivalents, $\varepsilon_i - \varepsilon_f$, listed in table 8 for the experiments in table 6 using Gua 1. The uncertainty in Group 1, where undissolved precipitate remained in the final solutions, was about one third of that in the other two groups. The large uncertainties in Groups 2 and 3 gives statistically questionable differences although the large difference between the means suggests a different reaction in the Group 3 experiments than in Group 2.

Table 8. Differences in energy equivalents for the initial and final systems ($\varepsilon_i - \varepsilon_f$) for the measurements of the enthalpy of solution of Gua 1 in HCl (see table 6).

Group		
1	2	3
	J/K	
0.22	0.57	-0.20
.21	.76	- .12
.45	.00	.16
.20	.07	- .52
.25	.17	- .17
.41	.79	.28
		- .09
		- .16
		- .78
[a]0.29 ± 0.04	[a] 0.39 ± 0.14	[a]- 0.18 ± 0.11

[a] Mean and standard deviation of the mean.

The values of $\Delta H(298.15\ \mathrm{K})$ as a function of HCl concentration for the experiments using Gua 1 (table 6) were fitted for each group by the method of least squares to linear, quadratic, and cubic equations. The resulting equations for the best fits are as follows (C is HCl concentration):

Group 1 ($C = 0.01$ to $0.2\ \mathrm{mol \cdot L^{-1}}$)
$\Delta H(298.15\ \mathrm{K}) = (0.04 \pm 0.43) + (229 \pm 13)(C) - (414 \pm 63)(C^2)$
Standard deviation of the fit $= 0.42\ \mathrm{kJ \cdot mol^{-1}}$.

Group 2 ($C = 0.3$ to $3.5\ \mathrm{mol \cdot L^{-1}}$)
$\Delta H(298.15\ \mathrm{K}) = (30.181 \pm 0.032) - (2.705 \pm 0.060)(C) - (0.237 \pm 0.015)(C^2)$
Standard deviation of the fit $= 0.025\ \mathrm{kJ \cdot mol^{-1}}$.

Combined Groups 2 and 3 ($\mathrm{C} = 0.3$ to $6.1\ \mathrm{mol \cdot L^{-1}}$)
$\Delta \mathrm{H}(298.15\ \mathrm{K}) = (30.28 \pm 0.19) - (2.85 \pm 0.16)(C) - (0.233 \pm 0.024)(C^2)$
Standard deviation of the fit $= 0.27\ \mathrm{kJ \cdot mol^{-1}}$.

Group 3 ($\mathrm{C} = 4.5$ to $6.1\ \mathrm{mol \cdot L^{-1}}$)
$\Delta \mathrm{H}(298.15\ \mathrm{K}) = (34.98 \pm 0.75) - (5.00 \pm 0.14)(\mathrm{C})$
Standard deviation of the fit $= 0.22\ \mathrm{kJ \cdot mol^{-1}}$.

The equation for the combined Groups 2 and 3 could be used, but it is believed that the use of separate equations is justified on the basis of the Δc_p and energy equivalent information discussed above. The two solid lines shown in figure 1 correspond to the equations for Groups 1 and 2, and the broken line, that for Group 3.

Beaven, et al [18], observed that adenine and guanine "have an additional pK in the region of pH 0." Our earlier work [5] reported evidence of such a protonation for adenine in HCl solution at the concentration, ∼ 5 $\mathrm{mol \cdot L^{-1}}$, with $\Delta H = (7.9 \pm 2.0)\ \mathrm{kJ \cdot mol^{-1}}$. Apparently a similar protonation for guanine occurs at the HCl concentration, 3.5 to 4 $\mathrm{mol \cdot L^{-1}}$ (see fig. 1). $\Delta H = (4.8 \pm 1.6)\ \mathrm{kJ \cdot mol^{-1}}$ was obtained from the difference between the intercepts of the equations for Group 3 and Group 2. The uncertainty is twice the sum of the standard deviations of the intercepts.

Several measurements of the enthalpy of solution using samples other than Gua 1 were made for comparison, and differences of about 10 percent (or more) in the values for ΔH were observed. These results are also shown in figure 1. The values measured for Gua 2 were close to those of Gua 1, but those for Gua 3, 4, and 4b (the latter was reprecipitated from Gua 4), were significantly smaller than those of Gua 1. In two experiments, the values for Gua 4b were higher than comparable values for Gua 4. This suggests that impurities were removed in the reprecipitation of Gua 4b.

3.2. ΔH_{soln} of Gua Hydrochlorides in Aqueous HCl

Measurements of the enthalpy of solution in aqueous HCl at various concentrations were made on four samples of guanine hydrochloride described in section 2 and the subsections. The calorimetric measurements were made on the dried samples some of which were hygroscopic; therefore, transfers to the sample holder were all made in a dry atmosphere. The elemental analyses indicated that the dried Gua·HCl 1 and 2c were probably the anhydrous monohydrochloride, and that Gua·HCl 2d was closer to the composition of the anhydrous hemihydrochloride; there was no elemental analysis of Gua·HCl 2a, but it was assumed to be similar to 2c (which was heated at a somewhat higher temperature).

The data obtained in the experiments where the enthalpies of solution of the guanine hydrochlorides were measured are given in table 9; the arrangement is in order of increasing HCl concentration. The molar enthalpies of solution at the reference temperature given in the last column assume the sample composition indicated by the elemental analyses. These molar enthalpies are plotted in figure 2 as a function of the concentration of the aqueous HCl; also shown for comparison are the curves obtained for Group 2 and Group 3 in figure 1. In figure 2, the points representing the values for a given sample of Gua·HCl are connected by straight lines. The 3 points for Gua·HCl 2d (assuming it is

Table 9. Data from the measurements of the enthalpy of solution of guanine hydrochloride in aqueous HCl solutions.

Expt.	Gua·HCl		HCl Soln.			Reaction Period	Electrical Energy Equivalent		$-\Delta T_{corr}$	$-Q_{obs}$	$-q_v$	$-Q_r$	T_r	[a]ΔH(298.15 K)	
No.	No.	Mass	[b]No.	Conc.	Mass		ϵ_i	ϵ_f							
		g		mol/L	g	min	J/K		K	J	J	J	K	J/g	kJ/mol
1065	1	0.23895	51	0.307	302.43	115	1711.35	1710.13	0.021708	37.137	0.03	37.11	297.992	155.31	26.30
1059	2c	.12225	52	.312	302.45	10	1710.91	1710.82	.012104	20.709	.04	20.67	297.950	169.08	28.64
1057	2d	.20510	52	.312	302.46	25	1710.93	1710.32	.021145	36.172	.03	36.14	297.993	175.46	32.91 (29.72)
1064	1	.22370	(62)	.998	302.46	10	1658.62	1658.36	.020052	33.256	.03	[c]33.26	298.019	148.68	25.18
1061	2c	.10652	(62)	2.83	307.50	30	1557.07	1556.11	.010003	15.570	.04	15.53	298.044	145.79	24.69
1060	1	.16306	(62)	2.84	307.64	20	1557.40	1557.23	.015960	24.856	.04	24.82	298.066	151.70	25.69
1062	1	.27484	(62)	4.00	307.61	55	1490.90	1490.40	.025175	37.527	.03	37.50	298.225	136.44	23.11
1063	1	.23858	(63)	4.99	307.45	25	1440.83	1440.62	.016145	23.260	.03	23.23	298.108	97.37	16.49
1056	1	.26366	60	5.01	307.40	20	1439.36	1439.60	.019347	27.850	.03	27.82	298.085	105.51	17.87
1055	2d	.18575	60	5.01	307.42	40	1439.05	1439.38	.011262	16.209	.03	16.18	298.111	87.10	16.34 (14.75)
1052	1	.21942	62	5.98	312.40	25	1410.82	1411.04	.016380	23.111	.03	23.08	298.102	105.19	17.82
1051	2a	.24960	61	5.98	312.42	135	1410.91	1411.02	.018812	26.543	.02	26.52	298.111	106.25	19.93
1053	2c	.10980	62	5.98	312.40	15	1410.46	1410.78	.008416	11.872	.04	11.83	298.101	107.74	18.25
1054	2d	.18211	62	5.98	312.43	35	1411.44	1411.13	.009121	12.872	.03	12.84	298.124	70.51	13.227 (11.941)

[a] The molar ΔH is calculated on the assumption that the samples are the anhydrous hydrochloride (molar mass = 187.5883). The numbers in parentheses are based on the assumption that sample 2d is the hemihydrochloride (molar mass = 169.3578) as indicated by the elemental analysis.

[b] The HCl soln No. indicates the stock solution from which the calorimetric solution was taken. Numbers in parentheses indicate that the calorimetric solution was prepared by dilution of the stock solution of the given number.

[c] This includes a correction, 0.026 J, for a brief departure of the temperature of the adiabatic shield from that of the reaction vessel because of the rapid reaction.

the hemihydrochloride) are on a straight line and the slope is nearly the same as that for Group 2 in figure 1. The values obtained assuming the monohydrochloride composition are further away from the Group 2 curve of figure 1. The values for Gua·HCl 1 and 2c lie on a horizontal straight line up to the HCl concentration ~ 4·mol·L^{-1}, but then there is a negative slope at the higher concentrations, somewhat analogous to that in figure 1. No conclusions can be drawn from these measurements because the molar quantities are based only on assumptions with respect to compositions. It does appear, however, that Gua·HCl 2d has different properties in solution than Gua·HCl 1 and 2c.

3.3. ΔH_{soln} of Gua in Aqueous NaOH

The results from 17 measurements of the enthalpy of solution of guanine in NaOH solutions are given in table 10 where the experiments are listed in order of increasing NaOH concentration. The sample masses are in the range 0.19 to 0.24 g (or 1.2 to 1.6 mmol of guanine), and the volume of the solvent is ~ 0.3 L. The reactions were all rapid and apparently complete; no residue was visible in the final solutions. In these experiments it was assumed that q_{vap} was negligibly small, because if the solutions were pure water q_{vap} would be < 0.05 J in the worst case (at 309 K); the actual corrections would be smaller than this since the vapor pressure of H_2O over the NaOH solutions is less than that over pure H_2O.

Values for Δc_p of the reaction in NaOH solutions (~ 0.1 mol·L^{-1}) were obtained from Expts. No. 971 and 972, 1.004 J·g^{-1}·K^{-1}, and from Expts. No. 895 and 896, 1.055 J·g^{-1}·K^{-1}. For calculating Corr$_{ST}$ the mean value, (1.03 ± 0.05) J·g^{-1}·K^{-1} was used; the uncertainty is estimated. The values may be different at the higher concentrations, but the work has terminated before other measurements could be made.

The values for the molar enthalpy of solution at the reference temperature, ΔH_m (298.15 K), from table 10 are plotted in figure 3 as a function of the concentration of the NaOH solution. Gua 1 was used for most of the measurements, but the numbers beside some of the points indicate the other guanine samples used (see sec. 2) for comparison. It can be

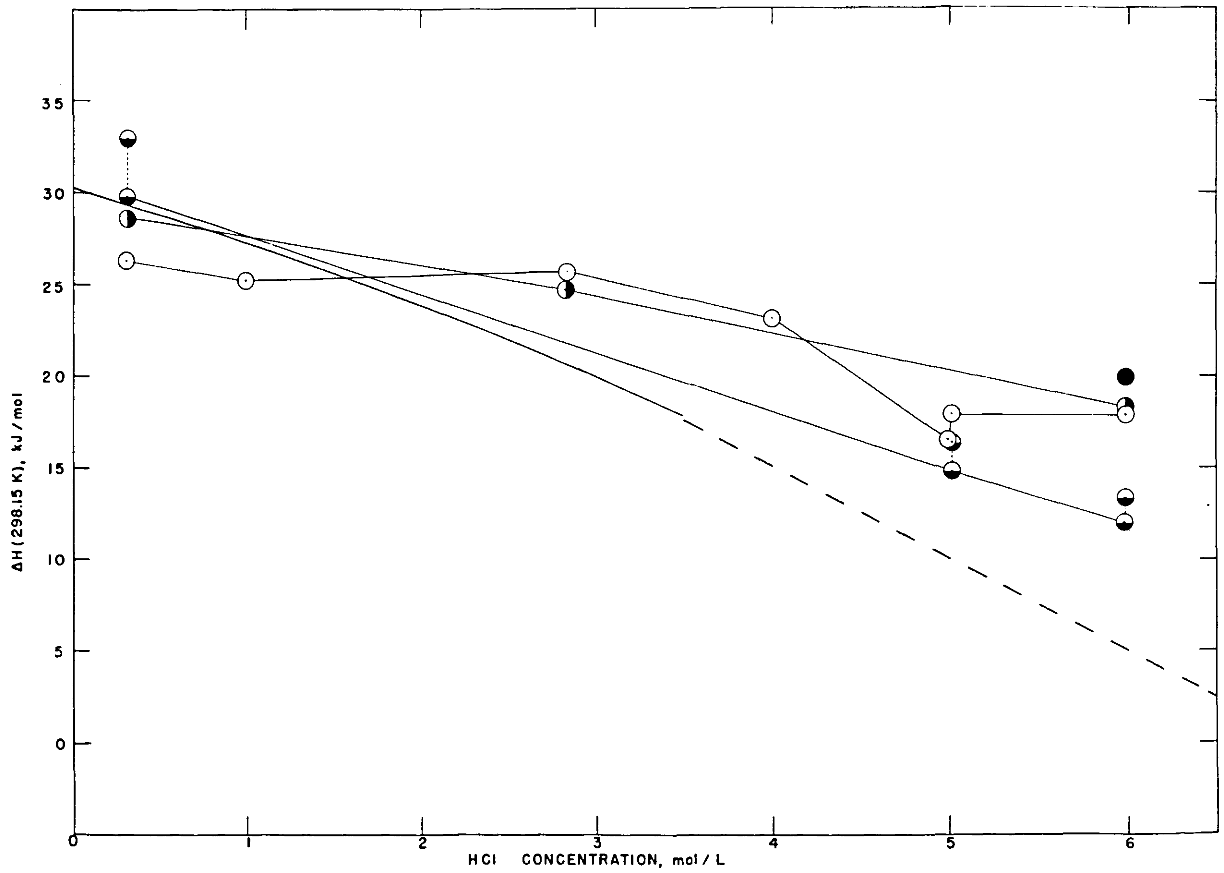


FIGURE 2. Plot of the values for the enthalpy of solution of various samples of guanine hydrochlorides as a function of the concentration of the solvent, aqueous HCl. The Gua·HCl samples are identified by the following symbols: ○, 1; ●, 2a; ◑, 2c; and ◒, 2d. The lower values of the points connected by dotted lines for Gua·HCl 2d were calculated assuming that the material was the hemihydrochloride (as indicated by the elemental analysis); the higher values were based on the assumption that the material was the monohydrochloride which appears to be an incorrect assumption. The curves from figure 1 are shown for comparison: Group 2, the solid line without data points, and Group 3, the broken line, without data points.

seen here that the values for Gua 2 were significantly less than those for Gua 1, but the values obtained in HCl solutions (see fig. 1) were nearly the same. Here the value for Gua 4 was close to those for Gua 1, but in the HCl solutions, Gua 4 showed a greater difference from Gua 1 than the other samples. Gua 4b, which was reprecipitated from Gua 4, had the lower values for the enthalpy of solution in aqueous NaOH; perhaps occluded water was not removed by drying.

A plot similar to figure 3 was previously given for adenine [5]. It showed no change of slope at ∼ 0.5 mol·L^{-1} as shown in figure 3; the reason for this difference is not known. For adenine, there was a change of slope (more negative) at the NaOH concentration, ∼ 4 mol·L^{-1}, which was assumed to be the result of a proton dissociation. Unfortunately, the guanine measurements terminated at ∼ 3 mol·L^{-1}, although a proton dissociation similar to that for adenine would be expected. The following equation was obtained from the fit of the data (table 10) for the 6 points above the NaOH concentration, C = 0.9 mol·L^{-1}, by the method of least squares to a linear equation:

$$\Delta H_m \text{ (298.15 K)} = (13.545 \pm 0.034) - (1.624 \pm 0.015)C.$$

The slope of this line is more negative than those from the adenine experiments, −0.36 and −0.89 kJ·mol^{-1}. The standard deviation of the fit is 0.036 kJ·mol^{-1}.

4. Discussion and Summary

Few measurements of the thermodynamic properties of guanine have been made. Stiehler and Huffman measured the heat of combustion [7], and the heat capacity [19] from which they calculated the entropy and free energy. The enthalpy of sublimation was measured by Yanson and Teplit-

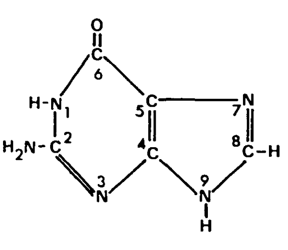
Table 10. Data from the measurements of the enthalpy of solution of guanine in aqueous NaOH solutions.

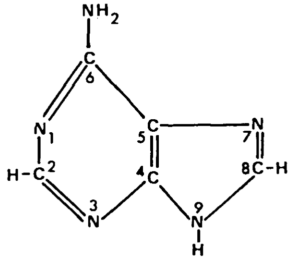
Expt. No.	Gua Sample	Gua [a]Mass	Soln. No.	NaOH Conc.	NaOH Mass	Reaction Period	Electrical Energy Equivalent ε_i	Electrical Energy Equivalent ε_f	$-\Delta T_{obs}$	$-Q_{obs}$	$-Q_r$	T_r	$Corr_{ST}$	ΔH_m(298.15 K)	ΔH_m(298.15 K)
		g		mol/L	g	min	J/K		K	J	J/g	K	J/g	J/g	kJ/mol
971	1	0.20668	44	0.0912	297.41	12	1709.88	1708.82	0.013536	23.138	111.95	298.226	0.08	111.87	16.91
972	1	.23756	44	.0912	302.40	12	1730.02	1730.00	.016860	29.167	122.78	309.009	11.18	111.60	16.86
895	1	.20809	35	.1010	303.62	7	1735.30	1734.67	.012994	22.545	108.34	298.208	0.06	108.28	16.36
896	1	.19833	35	.1010	303.64	5	1735.48	1735.21	.013658	23.702	119.51	308.795	10.96	108.55	16.40
973	1	.20837	42	.462	302.33	17	1704.99	1704.81	.010618	18.103	86.88	298.127	-0.02	86.90	13.13
894	1	.21029	36	.514	303.65	8	1707.49	1707.61	.01048	17.888	85.06	298.128	- .02	85.08	12.86
974	1	.21592	41	.919	302.20	12	1679.89	1679.70	.010263	17.240	79.84	298.140	- .01	79.85	12.07
1046	1	.20353	46	1.02	308.56	12	1699.42	1699.18	.009418	16.005	78.64	298.150	- .01	78.65	11.89
1048	4b	.20134	46	1.02	308.47	10	1698.46	1698.34	.009054	15.377	76.37	298.135	- .02	76.39	11.54
1045	1	.19545	45	1.33	308.56	7	1686.00	1685.90	.008716	14.694	75.18	298.146	.00	75.18	11.36
1047	4b	.19867	45	1.33	308.46	12	1686.01	1685.35	.008609	14.512	73.05	298.146	.00	73.05	11.04
1049	4	.19847	45	1.33	308.44	10	1685.36	1685.40	.008939	15.066	75.91	298.136	-.02	75.93	11.48
1050	2	.20435	45	1.33	308.47	10	1684.96	1685.26	.007805	13.153	64.37	298.240	.09	64.28	9.71
1050A	2	.19805	45	1.33	308.45	10	1685.62	1685.41	.007587	12.788	64.57	298.146	.00	64.57	9.76
975	1	.22021	43	2.83	307.15	12	1634.91	1634.75	.007988	13.059	59.30	298.153	.00	59.30	8.96
892	1	.19156	39	3.12	313.67	22	1654.22	1654.6	[b]-.511124	10.787	56.31	298.095	-.06	56.37	8.52
893	1	.19357	39	3.12	313.48	7	1653.23	1653.44	.006525	10.788	55.73	298.094	-.06	55.79	8.43

[a] Corrected for H_2O determined by vacuum drying other portions of the sample as follows: (Dried at 370 K) Gua 1, 1.01 % and Gua 4, 1.70 % (Dried at 340 K), Gua 2, 1.5 %. The Gua 4b samples had been dried at 340 K and no corrections were made for H_2O in the samples.

[b] Electrical energy added during the reaction = 856.405 J.

skii [20]. Measurements of pK values for protonation and proton dissociation by electrometric titration and by spectrophotometry were summarized by Izatt, et al. [21]. This review also discusses the protonation sites, N7 being the most likely, and the proton dissociation site, N1, in the guanine molecule. The structures of two of the purine bases, guanine and adenine, were given as





No values were reported for the enthalpy of protonation and only one value for the enthalpy of proton dissociation obtained from spectrophotometric measurements over large pH and temperature ranges. The value obtained by Suchorukow, et al. [22], may be described with the following equation which is analogous to those given for adenine [1]:

$$\mathrm{H_2Gua}(aq) = \mathrm{HGua^-}(aq) + \mathrm{H^+}(aq)$$
$$\Delta H(\infty, 298.15\ \mathrm{K}) = (42.2 \pm 2.1)\ \mathrm{kJ \cdot mol^{-1}}. \qquad (1)$$

Our measurements reported in section 3.3 result in

$$\mathrm{H_2Gua}(cr) + \mathrm{OH^-}(aq) = \mathrm{HGua^-}(aq) + \mathrm{H_2O}(l)$$
$$\Delta H(\infty, 298.15\ \mathrm{K}) = (13.545 \pm 0.034)\ \mathrm{kJ \cdot mol^{-1}}. \qquad (2)$$

Parker's selected value for $\Delta H_n°$ [17] can be represented by

$$\mathrm{H^+}(aq) + \mathrm{OH^-}(aq) = \mathrm{H_2O}(l)$$
$$\Delta H(\infty, 298.15\ \mathrm{K}) = -(55.84 \pm 0.10)\ \mathrm{kJ \cdot mol^{-1}}. \qquad (3)$$

If the sum of eq (1) and (3) is subtracted from eq (2), we obtain the enthalpy of solution of crystalline guanine at infinite dilution,

$$\mathrm{H_2Gua}(cr) = \mathrm{H_2Gua}(aq)$$
$$\Delta H(\infty, 298.15\ \mathrm{K}) = (27.2 \pm 2.1)\ \mathrm{Kj \cdot mol^{-1}}. \qquad (4)$$

Here and subsequently, the calculated uncertainty is the square root of the sum of the squares of the individual uncertainties.

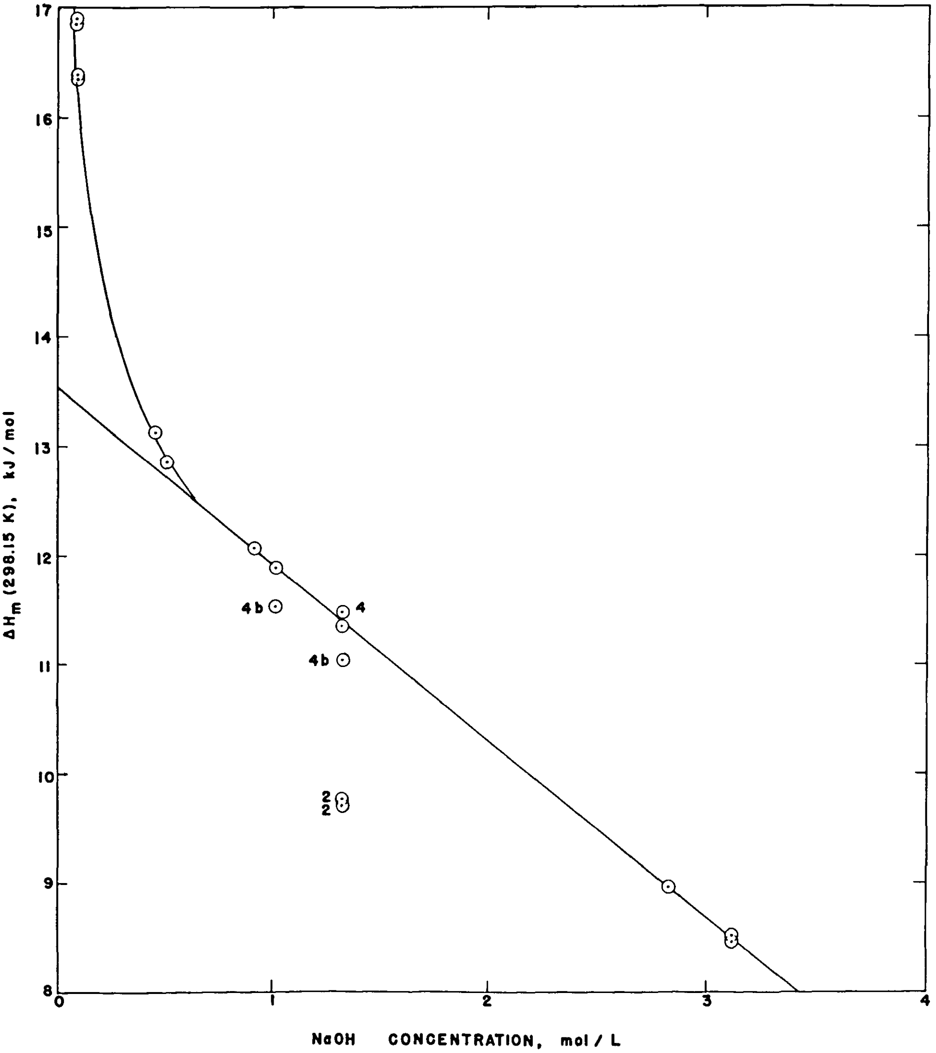


FIGURE 3. Plot of the enthalpy of solution of guanine as a function of the concentration of the solvent, aqueous NaOH. Gua 1 was used in all measurements except those with a number indicating the guanine sample used (see sec. 2).

Miller and Wasik [23] measured the solubility of our crystalline guanine sample, Gua 1, at three temperatures using a liquid chromatographic method developed by Wasik which is described elsewhere [24]. The guanine was first dissolved in methanol as a carrier liquid and transferred to the chromatographic column. The methanol was removed under vacuum, liquid water was introduced for saturation by the guanine deposit, and the guanine concentration in the saturated solution was determined chromatographically. The results are as follows: mean of 3 measurements at 292 K, (5.0 ± 0.2) × 10^{-4}mol·L^{-1}; mean of 8 measurements at 298 K, (6.0 ± 0.2) × 10^{-4}mol·L^{-1}; and mean of 3 measurements at 303 K, (8.7 ± 0.3) × 10^{-4}mol·L^{-1}. The uncertainties are the average deviations. The enthalpy of solution, ΔH, may be calculated from the solubilities using the van't Hoff equation,

$$\frac{d\ ln\ s}{dT}=\frac{\Delta H}{RT^2},$$

where s is the solubility, T is the absolute temperature, and R is the gas constant. Assuming the ΔH is linear with temperature we calculate a value of ~ 36 kJ·mol^{-1} at 298 K. This is in disappointingly poor agreement with our value at infinite dilution calculated in equation (4), which would probably be nearly the same as the value at saturation because the solubility is extremely low. It is possible that some chemical change in the guanine occurred when it was dissolved in methanol, and that the measurements were actually made on a derivative of guanine. Therefore, a second set of measurements were made in which the presolution in methanol was by-passed. A saturated aqueous solution was introduced directly into the column and its concentration was determined. Three measurements were made at each of three temperatures and the average solubilities are as follows: 3.5×10^{-4} mol·L^{-1} at 293 K, 4.5×10^{-4}mol·L^{-1} at 298 K, and 4.8×10^{-4}mol·L^{-1} at 303 K. The average deviations were less than 1×10^{-5}mol·L^{-1}. $\Delta H = 22$ kJ·mol^{-1} was calculated by the above method. This is *lower* than our value in eq (4), possibly because of the difficulty in saturating the solution. It is noteworthy that the solubilities in water were different if the guanine was pretreated in methanol.

In reference [21] evidence was given for the protonation at *N*7. Our measurements in section 3.1 show, in addition, a second protonation (probably at N3) at pH < 1. These correspond to the following equations:

$$H_2Gua(cr) + H^+(aq) = H_3Gua^+(aq)$$
$$\Delta H(\infty, 298.15\ K) = (30.181 \pm 0.032)\ kJ \cdot mol^{-1}, \tag{5}$$

and

$$H_2Gua(cr) + 2H^+(aq) = H_4Gua^{2+}(aq)$$
$$\Delta H(\infty, 298.15\ K) = (34.98 \pm 0.75)\ kJ \cdot mol^{-1}. \tag{6}$$

By subtracting eq(4) from eq(5) and from eq(6), we obtain

$$H_2Gua(aq) + H^+(aq) = H_3Gua^+(aq)$$
$$\Delta H(\infty, 298.15\ K) = (3.0 \pm 2.1)\ kJ \cdot mol^{-1}, \tag{7}$$

and

$$H_2Gua(aq) + 2H^+(aq) = H_4Gua^{2+}(aq)$$
$$\Delta H(\infty, 298.15\ K) = (7.8 \pm 2.2)\ kJ \cdot mol^{-1}. \tag{8}$$

Equation (7) corresponds to the protonation of *N*7 and eq (8) presumably to the protonation of both *N*7 and *N*3. No other values have been reported previously for these reactions.

Analogous enthalpy of solution values obtained for adenine in [1] and for guanine in this work are summarized in table 11. A summary of values measured for ΔC_p of reaction for adenine and guanine are given in table 12.

The results reported here have shown the need for thorough characterization of the samples used in precise calorimetric measurements. More work is needed before reliable values for the guanine hydrochlorides can be given.

Table 11. Summary of analogous values for enthalpies of solution, protonation, and proton dissociation for the purine bases, adenine and guanine.

Equation (P = purine base, Ade or Gua)	$\Delta H(\infty$, 298.15 K)	
	Ade[1]	Gua [This work]
	kJ/mol	
$H_2P(cr) + aq = H_2P(aq)$	33.47	[a] 2.72
$H_2P(cr) + H^+(aq) = H_3P^+(aq)$	11.41	30.181
$H_2P(cr) + 2\ H^+(aq) = H_4P^{2+}(aq)$	19.3	34.98
$H_2P(cr) + OH^-(aq) = HP^-(aq) + H_2O(\ell)$	15.207	13.545
$H_2P(cr) + 2\ OH^-(aq) = P^{2-}(aq) + 2\ H_2O(\ell)$	17.26	---
$H_2P(aq) + H^+(aq) = H_3P^+(aq)$	-22.1	[a]3.0
$H_2P(aq) + 2\ H^+(aq) = H_4P^{2+}(aq)$	-14.2	[a]7.8
$H_2P(aq) = HP^-(aq) + H^+$	[a] 37.58	[b](42.2)
$H_2P(aq) = P^{2-}(aq) + 2\ H^+$	[a] 95.47	---

[a] Calculated using auxiliary data (other values obtained by direct measurements).

[b] Obtained by Suchorukow, et al. [22].

Table 12. Summary of values of the ΔC_p of reaction measured for adenine and guanine in various solvents at 298 K. (Uncertainties are estimated except as noted).

Solvent	Ade [1,5]		Gua [this work]	
	Solvent Conc.	ΔC_p	Solvent Conc.	ΔC_p
	mol/L	J/mol·K	mol/L	J/mol·K
HCl			0.1	814 ± 75
	1.0	107 ± 3	0.3 to 3.5	98 ± 8
			∿ 6	160 ± 15
NaOH	0.9	126 ± 8	0.1	156 ± 8
H_2O	---	[a]78.7 ± 10.4	---	---

[a] Uncertainty is at the 95 % confidence level.

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Player Aggregation in Noncooperative Games, II*

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Conditions are given under which subsets of the players of a noncooperative game can be combined into "aggregate players" without changing the set of equilibrium-point solutions of the game. These conditions are shown to be the weakest possible ones with a certain specified kind of generality. "Approximate" versions of the results are also formulated and proven.

Key words: Aggregation; equilibrium; game theory; mathematical economics; noncooperative games; total orders.

1. Introduction

Like its predecessor [1],[1] this paper is motivated by the following observation: in applied game-theoretic modeling, it may prove useful to reduce model-complexity and data-needs by combining, into a single "aggregate player," some subset of the original players whose interests are sufficiently "parallel" for this purpose. It is natural, therefore, to investigate from a mathematical viewpoint the conditions under which such an aggregation is "valid" in the sense of leaving the game's set of "solutions" undisturbed. Results of this type were needed, for example, in connection with a class of models [2, 3, 4] involving an inspection agency with insufficient resources to visit all of a number of sites at which "cheating" might or might not occur; the issue was whether the individual site-managers could be aggregated into a single "inspectee" entity so that the situation could be analyzed as a two-person game.

Our treatment here is limited to noncooperative games and to the equilibrium-point notion of "solution." For completeness, these concepts are defined in section 2 below, where the process of aggregation is also formalized. A natural special case of aggregation ("group equilibrium") is discussed in [5], but without considering the question of solution-set preservation.

In [1], a simple condition was given under which aggregation does not change a game's set of solutions. That condition stated that each individual player's payoff (in the original game) is independent of the strategy choices by the other individuals comprising the same aggregate player. Though applicable to the inspector-inspectee games mentioned above, this condition is clearly rather restrictive, and captures the "independence" or "indifference" of the aggregated players' interests rather than (as desired) the "parallelism" of those interests. In section 3 of the present paper, we give less restrictive sufficient conditions for aggregation (a) to avoid introducing extraneous solutions, and (b) to preserve all solutions of the original game. Further theorems and examples show that these conditions, though not necessary as well as sufficient, are actually the weakest possible sufficient conditions with a certain specified kind of generality. Additional examples show that the family of player-subsets which are "aggregable," in the sense of obeying the minimal conditions mentioned above, need not have certain properties to be expected if aggregability fully corresponded to some natural notion of "parallel interest;" for example, a subset of an aggregable set need not be aggregable.

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[1] Numbers in brackets indicate literature references at the end of the paper.

Consistent with [1], section 4 extends the preceding material to "approximate solutions" in cases in which the conditions described above are satisfied only approximately. This topic reflects an expectation that in applied contexts, many mathematical relationships will not (or cannot be known to) hold exactly.

I am grateful to colleague D. R. Shier, whose careful reading of a first version of this paper revealed the need for several corrections and clarifications.

2. Games, equilibria, aggregation

Let $n \geqslant 1$ be an integer, and $N = \{1,2,\ldots,n\}$. An n-person noncooperative game $G = (X, f)$ consists of an n-tuple $(X_1, \ldots, X_n)$ of nonempty sets X_i with Cartesian product X, and an n-tuple $f = (f_1, \ldots, f_n)$ of functions f_i: $X \rightarrow R_i$ where R_i is equipped with a strict linear order ϱ_i. Here X_i is interpreted as the set of strategies or actions open to the i-th player, f_i as that player's "payoff function," R_i as the set of possible payoffs or outcomes experienced by that player, and ϱ_i as the relation of (strict) preference by that player among outcomes. The fact that the domain of f_i is X, rather than X_i, expresses the idea that each player's payoff depends not only on what strategy that player chooses, but also on the choices made by other players.

For any $x \varepsilon X$, any $i \varepsilon N$, and any $x_i \varepsilon X_i$, we denote by (x, i, x_i) the member of X obtained from x by changing its i-th coordinate to x_i. With this notation, a "solution" concept can be defined: $x^\circ \varepsilon X$ is called an *equilibrium point* (*EP*) for game G if, for every $i \varepsilon N$ and every $x_i \varepsilon X_i$, the relation

$$f_i(x^\circ, i, x_i)\, \varrho_i\, f_i(x^\circ) \tag{1}$$

is *false*. That is, if one thinks of the coordinates of x° as the players' "current" choices of strategies, then no player has an incentive to deviate unilaterally from his or her current choice. Since the game is regarded as "noncooperative," only unilateral shifts come into consideration, and so the falsity of all relations (1) is sufficient to describe the "stability" of x°. If $n = 1$, an *EP* is simply a strategy that yields a preference-maximal outcome for the (sole) player.

Next we describe an "aggregation" of game G. Let m be an integer with $1 \leqslant m \leqslant n$, and let $M = \{1, 2, \ldots, m\}$. An m-player aggregation $G[B,F]$ of G is specified by the following structure. $B = \{B_1, \ldots, B_m\}$ is a partition of N into nonempty sets; note that the relation $i \varepsilon B_{j(i)}$ defines a function j: $N \rightarrow M$. Let S_j be the Cartesian product of the sets $\{R_i : i \varepsilon B_j\}$; also let $F = (F_1, \ldots, F_m)$ be an m-tuple of functions $F_j : S_j \rightarrow T_j$ where each set T_j is equipped with a strict linear order τ_j, and function F_j is strictly monotone in each of its arguments. This last condition means that for any $s_j \varepsilon S_j$, for any $i \varepsilon B_j$ with r_i the i-th coordinate of s_j, and for any $r'_i \varepsilon R_i$,

$$r'_i \varrho_i r_i \text{ implies } F_j(s_j, i, r'_i)\, \tau_j\, F_j(s_j). \tag{2}$$

Such a structure defines an m-person game as follows. The "players" are $\{B_j : j \varepsilon M\}$. The set of strategies of B_j is Y_j, the Cartesian product of $\{X_i : i \varepsilon B_j\}$. Note that the Cartesian product of the player's strategy-sets, i.e. of $\{Y_j : j \varepsilon M\}$, is the same set X as for the original game; this permits the symbols "x" and "y" to be used interchangeably, and corresponds to the idea that we are dealing with aggregation of players and payoffs, but not of strategies. (The same observation justifies the later use of notation like (x, j, y_j), as an extension of the previous symbol (x, i, x_i).) In the aggregated game, the payoff function for player B_j is g_j : $X \rightarrow T_j$, defined by[2]

$$g_j(x) = F_j[\{f_i(x) : i \varepsilon B_j\}]. \tag{3}$$

The definition of an *EP* for game $G[B,F]$ is directly analogous to that for G.

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[2] In the following notation, the argument of F_j is the member $s_j \varepsilon S_j$ whose i-th coordinate, for $i \varepsilon B_j$, is $f_i(x)$.

3. Preservation of the solution-set

For any subset S of N, let X_S denote the Cartesian product of the strategy-sets $\{X_i : i \varepsilon S\}$. We will call $x \varepsilon X$ *S-stable* if there is no $x_S \varepsilon X_S$ such that (with an obvious extension of previous notation)

$$f_i\,(x,S,x_S)\varrho_i f_i(x) \text{ or } f_i\,(x,S,x_S) = f_i(x)$$

holds for each $i \varepsilon S$, with the first relation holding for at least one $i \varepsilon S$. Intuitively, this means that even if the players in S could act together, they could effect no deviation from the *status quo* represented by x which would be "advantageous to S" in the sense of being preferable to some members of S and a matter of indifference to the others. Thus x° is an *EP* if and only if it is $\{i\}$-stable for all $i \varepsilon N$.

Let X^S denote the set of S-stable members of X. We call S *nonfrustrating* (*NF*) if

$$X^S \subseteq \cap \{X^{\{i\}} : i \varepsilon S\}. \tag{4}$$

The reason for this terminology is best seen by taking complements in (4): for each $x \varepsilon X$, if some player $i \varepsilon S$ can find a unilateral deviation preferable (for i) to the *status quo* represented by x, then there is a joint deviation $x_S \varepsilon X_S$ which is "advantageous to S" in the sense described above and which could therefore be adopted by S without internal dissension were it the only available alternative to continuation of x. That is, there is no opposition of interests within S that would preclude deviating from a *status quo* which some single player in S could profitably deviate from. Thus no player, by becoming part of an aggregate player S, would risk the frustration of being "stuck with" an undesirable *status quo* against which he or she had a unilateral counteraction as an individual player.

THEOREM 1. *If each* B_j *is* NF *and* x° *is an* EP *for* G [B,F], *then* x° *is also an* EP *for* G.

PROOF. Suppose, to the contrary, that (1) holds for some $i \varepsilon N$. Then x° is not in $X^{\{i\}}$; since $B_{j(i)}$ is NF, x° cannot be $B_{j(i)}$-stable. Thus there exists $y_{j(i)} \varepsilon Y_{j(i)}$ such that changing from x° to $(x^\circ, j(i), y_{j(i)})$ is "advantageous to $B_{j(i)}$" in the sense defined above. Consider changing the arguments of $F_{j(i)}\,[\{f_k\,(x^\circ) : k \varepsilon B_{j(i)}\}]$ one at a time to those of $F_{j(i)}[\{f_k\,(x^\circ, j(i), y_{j(i)}) : k \varepsilon B_{j(i)}\}]$; by the monotonicity of $F_{j(i)}$ and the transitivity of $\tau_{j(i)}$ it follows—cf. (3)—that $g_{j(i)}\,(x^\circ, j(i), y_{j(i)})\tau_{j(i)}\, g_{j(i)}(x^\circ)$, contradicting the hypothesis that x° is an *EP* for $G[B,F]$.

We will call a subset S of N *unilateral-deviation unanimous* (*UDU*) if, for each $x \varepsilon X$ and $i \varepsilon S$, any $x_i \varepsilon X_i$ for which $f_i(x,i,x_i)\varrho_i f_i(x)$ also has the property that

$$f_k(x,i,x_i)\varrho_k f_k(x) \text{ or } f_k(x,i,x_i) = f_k(x)$$

holds for all $k \varepsilon S - \{i\}$. Intuitively, this says that whenever a single player in S has incentive for some particular unilateral deviation from a *status quo*, then no other player in S would regret seeing that single deviation effected. This condition, introduced only for the sake of the following Corollary, may be easier to recognize than NF.

COROLLARY. *If each* B_j *is* UDU, *and* x° *is an* EP *for* G[B,F], *then* x° *is also an* EP *for* G.

PROOF. In view of Theorem 1, it suffices to observe that UDU implies NF; the proof of that implication is straightforward.

As preparation for the next result, observe that condition NF when applied to subset S of N is "local to S," in that it does not refer to the attributes $\{R_i, \varrho_i, f_i\}$ of the players $i \varepsilon N\text{-}S$. This is important for ease of checking the condition. Furthermore, *NF* is "general" in that it does not refer to the attributes (T_S, τ_S, F_S) of S as an aggregate player in any particular aggregated version of G. The next theorem shows that condition *NF* is the *weakest* one, with these two properties, which would suffice for an analog of Theorem 1.

THEOREM 2. *Let all the information needed to define* G *and* $G[B,F]$ *be specified except for* (T_1,τ_1,F_1) *and* $\{f_i : i\varepsilon N\text{-}B_1\}$. *If* B_1 *is not* NF, *then the missing information can be specified in such a way that* $G[B,F]$ *has an* EP *which is not an* EP *for* G.

PROOF. Since B_1 is not *NF*, there exists a B_1-stable $x\varepsilon X$, an $i\varepsilon B_1$, and an $x_i\varepsilon X_i$, such that

$$f_i(x,i,x_i)\varrho_i f_i(x). \tag{5}$$

It follows from (5) that x cannot be an *EP* for G. We shall specify the missing information in such a way that x is an *EP* for $G[B,F]$.

Choose each of $\{f_t : t\varepsilon N\text{-}B_1\}$ to be constant, and write "$B(1)$" instead of "B_1" for subscripting purposes. For x to be an *EP* for $G[B,F]$, it suffices to choose (T_1,τ_1,F_1) in such a way that for no $x_{B(1)}\,\varepsilon X_{B(1)}$ is

$$F_1[\{f_p(x,B_1,x_{B(1)}) : p\varepsilon B_1\}]\tau_1 F_1[\{f_p(x) : p\varepsilon B_1\}]. \tag{6}$$

Choose $T_1 = S_1$, and F_1 to be the identity map of S_1. Define τ_1^* as the direct product of $\{\varrho_p : p\varepsilon B_1\}$; that is, given s_1 and s_1' in S_1, with respective coordinates $\{r_p : p\varepsilon B_1\}$ and $\{r_p' : p\varepsilon B_1\}$, then $s_1'\tau_1^* s_1$ holds if and only if

$$r_p'\varrho_p r_p \text{ or } r_p' = r_p$$

holds for all $p\varepsilon B_1$, with the former relation holding for at least one $p\varepsilon B_1$. This τ_1^* is a strict partial order on T_1, but not in general a linear order. To make F_1 strictly monotone in each of its arguments, as required, we must (and it suffices to) choose the linear order τ_1 to be an extension of τ_1^*.

The partial order τ_1^* can be viewed as a collection of ordered pairs of distinct members of T_1, where $(t,t')\,\varepsilon T_1 \times T_1$ is in the collection if and only if $t\tau_1^* t'$. Now let t° be the member of T_1 with coordinates $\{f_p(x): p\varepsilon B_1\}$, and for each $x_{B(1)}\varepsilon X_{B(1)}$ let $h(x_{B(1)})$ be the member of T_1 with coordinates $\{f_p(x,B_1,x_{B(1)}) : p\varepsilon B_1\}$. Define a second collection of ordered pairs by

$$T^{\circ} = [h(X_{B(1)}) - \{t^{\circ}\}] \times \{t^{\circ}\}.$$

Then the fact that x is B_1-stable can be written as $T^{\circ} \cap \tau_1^* = \phi$, and the desired condition that (6) hold for no $x_{B(1)}\varepsilon X_{B(1)}$ can be written $T^{\circ} \cap \tau_1 = \phi$.

What remains to be proved, then, is the existence of a strict linear order τ_1 on T_1 which is an extension of τ_1^* and which satisfies $T^{\circ} \cap \tau_1 = \phi$. Since in general $T^{\circ} \neq \phi$, we cannot simply appeal to the general theorem [6] that every partial order can be extended to a linear order. Let T be the family of all strict partial orders on T_1 which contain τ_1^* and are disjoint from T°. T is not empty, since it includes τ_1^*. Considered as subsets of $T_1 \times T_1$, the members of T are partially ordered by set-inclusion, and the union of any linearly-ordered subfamily of T is easily shown to be again in T. By Zorn's Lemma, T has a maximal member τ_1. The proof will be completed by showing that τ_1 is a linear order.

Suppose, to the contrary, that there exist distinct elements t,t' of T_1 such that neither (t,t') nor (t',t) lies in τ_1. (It is in the balance of this paragraph that a more delicate argument than that given in [6] for the case $T^{\circ} = \phi$ is required.) At most one of t,t' can coincide with t°; if one of them does, choose the notation for t and t' so that $t = t^{\circ}$ and $t' \neq t^{\circ}$. Observe that at least one of (t,t') and (t',t) must fail to be a (t'',t''') with the property that $(t'',t^{\circ})\varepsilon\tau^{\circ}$ and $(t''',t^{\circ})\varepsilon\tau_1$ (this is true because $T^{\circ} \cap \tau_1 = \phi$); if either (t,t') or (t',t) is a (t'',t''') with the property just mentioned, choose the notation for t and t' so that (t',t) rather than (t,t') is such a (t'',t'''). (This precaution will only be needed if neither t nor t' coincides with t°.) Note for future use that in this case, there cannot be an $s\varepsilon T_1$ such that $(s,t)\varepsilon\tau_1$, $(t',t^{\circ})\varepsilon\tau_1$ and $(s,t^{\circ})\varepsilon T^{\circ}$. Observe further that at least one of (t,t') and (t',t) must fail to be a $(\bar{t}'',\bar{t}''')$ with the property that for some $s\varepsilon T_1$, the relations $(s,\bar{t}'')\varepsilon T_1$, $(\bar{t}''',t^{\circ})\varepsilon\tau_1$ and $(s,t^{\circ})\varepsilon T^{\circ}$ all hold. In this case, choose the notation for t and t' so that (t,t') is not a $(\bar{t}'',\bar{t}''')$ with the last-mentioned property. (This precaution will only be needed if neither t nor t' coincides with t°, and if in addition neither (t,t') nor (t',t) is a (t'',t''') of the type described above.)

Now set

$$\bar{\tau}_1 = \tau_1 \cup \{(t,t')\} \cup \{(s,t'): (s,t)\in\tau_1\} \cup \{(t,s'): (t',s')\in\tau_1\}$$

$$\cup \{(s,s'): (s,t), (t',s')\in\tau_1\}.$$

Then $\bar{\tau}_1$ is a binary relation on T_1 which is a proper extension of τ_1. A straightforward enumeration of cases, ignoring the care with which the notation for t and t' was chosen above, verifies that $\bar{\tau}_1$ is a strict partial order on T_1. With that care taken into account, another enumeration of cases verifies that $T^0 \cap \bar{\tau}_1 = \phi$, yielding a contradiction to the maximality of τ_1 in T. So τ_1 is a linear order, and Theorem 2 is proved.

Having considered what conditions rule out the introduction through aggregation of "extraneous" solutions (*EP*'s), we now turn to ruling out the *loss* of solutions under aggregation. A subset S of N will be called *unilateral-deviation strong* (*UDS*) if for each $x\in X$, in case $f_k(x,S,x_S)\varrho_k f_k(x)$ holds for any $k\in S$ and $x_S\in X_S$, it follows that $f_i(x,i,x_i)\varrho_i f_i(x)$ for some $i\in S$ and $x_i\in X_i$. This (somewhat unsatisfactory) terminology is intended to reflect the idea that the unilateral deviations desirable to the individual members of S (as deviators) are, taken together, sufficiently "strong" to reject any *status quo* x from which S as a collective could possibly deviate to the advantage of *any* of its members.

THEOREM 3. *If each* B_j *is* UDS, *and* x° *is an* EP *for* G, *then* x° *is also an* EP *for* G[B,F].

PROOF. Suppose, to the contrary, that $g_j(x^\circ,j,y_j)\tau_j g_j(x^\circ)$ for some $j\in M$ and some $y_j\in Y_j$. Because each of $\{\varrho_k : k\in B_j\}$ is a linear order and F_j is monotone, it follows (proof by contradiction) that

$$f_k(x^\circ,j,y_j)\varrho_k f_k(x^\circ)$$

must hold for at least one $k\in B_j$. From this, and the fact that B_j is *UDS*, there follows immediately a contradiction to the hypothesis that x° is an *EP* of *G*.

Note that *UDS*, applied to subset S of N, has the same "local to S" and "generality" properties described before Theorem 2. The next theorem shows that *UDS* is the *weakest* condition, with these two properties, which would suffice for an analog of Theorem 3.

THEOREM 4. *Let all the information needed to define* G *and* G[B,F] *be specified except for* $(\mathrm{T}_1,\tau_1,\mathrm{F}_1)$ *and* $\{\mathrm{f}_i : i\in\mathrm{N} - \mathrm{B}_1\}$. *If* B_1 *is not* UDS, *then the missing information can be specified in such a way that* G *has an* EP *which is not an* EP *for* G[B,F].

PROOF. Write "$B(1)$" instead of "B_1" for subscripting purposes. Since B_1 is not *UDS*, there exists an $x\in X$, an $x_{B(1)}\in X_{B(1)}$, and a $k\in B_1$ such that

$$f_k(x,B_1,x_{B(1)})\varrho_k f_k(x), \tag{7}$$

$$f_i(x,i,x_i)\varrho_i f_i(x) \text{ for no } i\in B_1 \text{ and } x_i\in X_i. \tag{8}$$

Choose each of $\{f_t : t\in N - B_1\}$ to be constant; then (8) implies that x is an *EP* for *G*. Choose $T_1 = S_1$, and F_1 to be the identity map of S_1. Let $|B_1| = b$, and let $\{k(1),k(2),\ldots,k(b)\}$ be any enumeration of B_1 in which $k(1) = k$. Take τ_1 to be the lexicographic product of the sequence $\{\varrho_k = \varrho_{k(1)},\varrho_{k(2)},\ldots,\varrho_{k(b)}\}$; then τ_1 is a linear order and F_1 is monotone. It follows from (7) that $g_1(x,B_1,x_{B(1)})\tau_1 g_1(x)$, and so x cannot be an *EP* for *G*[*B,F*], completing the proof.

Combining the previous results, we see that if each B_j is both *NF* and *UDS*, then *G*[*B,F*] has the same set of *EP*'s as *G*. Furthermore, the conjunction "*NF* and *UDS*" is the *weakest* condition, with the properties of being "local" and "general" as defined earlier, which suffices for such a conclusion; one might well refer to this condition as "aggregability." The question of how this condition might be systematically and efficiently checked-for is a natural one, but will not be addressed here.

To relate the preceding material to that of [1], we define a subset S of N to be *limited-dependent* (*LD*) if, for each $i \varepsilon S$, $f_i(x)$ does not depend on the coordinates of x associated with the players in $S - \{i\}$. Theorems 1 and 2 of [1] are then equivalent to the following assertion.

THEOREM 5. *If each* B_j *is* LD, *then* $G[B,F]$ *has the same set of* EP's *as* G.

PROOF. By Theorems 1 and 3, it suffices to show, if S is an *LD* subset of the players, that S is both *UDU* (hence, *NF*) and *UDS*. First, suppose some $x \varepsilon X$ is not $\{i\}$-stable for some $i \varepsilon S$, i.e. $f_i(x,i,x_i)\varrho_i f_i(x)$ for some $x_i \varepsilon X_i$. Since S is *LD*, $f_k(x,i,x_i) = f_k(x)$ for all $k \varepsilon S - \{i\}$. This shows that S is *UDU*. Next, consider any $x \varepsilon X$ such that $f_k(x,S,x_S)\varrho_k f_k(x)$ for some $k \varepsilon S$ and $x_S \varepsilon X_S$. Let x_k be the coordinate of x_S corresponding to player k; since S is *LD*, $f_k(x,S,x_S) = f_k(x,k,x_k)$ and so $f_k(x,k,x_k)\varrho_k f_k(x)$. This shows that S is *UDS*, completing the proof of the theorem.

To show that Theorem 5's sufficient condition for preservation of the solution-set was not also a necessary condition, the following example was given in [1]. It had $n = 2$, $m = 1$, and $B_1 = \{1,2\}$. Each $\varrho_i (i = 1,2)$ was the numerical ">" relation, $X_1 = \{A,B\}$, $X_2 = \{a,b\}$, and the payoff functions f_1 and f_2 were identical ($f_1 = f_2 = \bar{f}$) with

$$\bar{f}(A,a) = 2, \bar{f}(A,b) = \bar{f}(B,a) = 1, \bar{f}(B,b) = 0.$$

Here B_1 is not *LD*, but both G and $G[B,F]$—for any choice of (T_1,τ_1,F_1)—have (A,a) as the unique equilibrium point. It is easily verified that B_1 is both *NF* and *UDS*, so that this example is "explained" by Theorems 1 and 3 of the present paper.

To illustrate that the hypotheses of Theorems 1 and 3, though sufficient conditions for the Theorems' conclusions to hold, are not also necessary conditions, we will give an example in which *NF* and *UDS* both fail, but G and $G[B,F]$ have the same set of equilibrium points. We would like the set of G's equilibrium points to be a *proper* subset of X (so that aggregation has a fair chance to introduce one or more extraneous *EP*'s), and to be nonempty (so that aggregation has a fair chance to lose one or more *EP*'s). Also, to keep the example simple, we would like to have $n = 2$, $m = 1$, and $B_1 = \{1,2\} = N$. For an example meeting all these stipulations, take $(X_1,X_2,\varrho_1,\varrho_2)$ as in the last paragraph, but set

$$f_1(A,a) = 1, f_1(B,a) = 2, f_1(A,b) = f_1(B,b) = 0$$

and $f_2 = -f_1$. Then (in the notation introduced above eq (4)) $X^{\{1\}} = X - \{(A,a)\}$ and $X^{\{2\}} = \{(A,b), (B,b)\}$. Because G is zero-sum, $X^{\{1,2\}}$ is all of X, and comparison with (4) shows that *NF* fails. That *UDS* fails can be seen from the statement of this condition by taking $k = 1$, $x = (A,b)$, $x_S = (B,a)$. The set of equilibrium points of G is given by $X^{\{1\}} \cap X^{\{2\}} = X^{\{2\}}$, a nonempty proper subset of X. Now take $T_1 = S_1$, F_1 to be the identity map of T_1, and τ_1 to be the lexicographic product of the ordered pair (ϱ_2,ϱ_1); with this choice, $G[B,F]$ has the same equilibrium-point set as G.

In the remainder of this Section, we investigate how well the conditions appearing above—*NF, UDU, UDS,* "*NF* and *UDS*," and *LD*—conform to some intuitively plausible requirements for representing the notion of "parallel interests." Let $\mathcal{F}$ be a family of nonempty subsets of N, which includes all singletons. We will say that $\mathcal{F}$ is *equivalence-derived* if there is an equivalence relation on N such that subset S of N belongs to $\mathcal{F}$ if and only if S lies in a single equivalence class. Also, we will call $\mathcal{F}$ *hereditary* if $\emptyset \neq T \subset S$ and $S \varepsilon \mathcal{F}$ imply $T \varepsilon \mathcal{F}$, and will call $\mathcal{F}$ *connected* if $S \varepsilon \mathcal{F}$, $T \varepsilon \mathcal{F}$ and $S \cap T \neq \emptyset$ imply $S \cup T \varepsilon \mathcal{F}$. All three of these properties are plausible requirements if $\mathcal{F}$ is to represent the family of all subsets whose players "have parallel interests." It is easy to show that a family $\mathcal{F}$ is equivalence-derived if and only if it is both hereditary and connected, so that we will deal with these last two properties.

None of the conditions appearing in the previous theorems necessarily yields a connected family of subsets of N. To show this, it suffices to give an example in which subsets S and T of the players are both *LD* (hence *NF, UDU* and *UDS*), satisfy $S \cap T \neq \emptyset$, but have $S \cup T$ neither *NF* nor *UDS*. Such an example can be constructed from the preceding one by adjoining a third player as "dummy." Specifically, take $(X_1,X_2,\varrho_1,\varrho_2)$ as before; (X_3,ϱ_3) need not be specified, for what follows. Adjoin a dummy argument $x_3 \varepsilon X_3$ to the previous definitions of f_1 and f_2, and take f_3 to be constant. Choosing $S = \{1,3\}$ and $T = \{2,3\}$ then yields an example with the desired characteristics.

It is easily shown that the *LD* subsets of N form a hereditary family, as do the *UDU* subsets. To dispose of the "hereditary question" for the remaining properties, it suffices to give an example in which subsets S and T of the players satisfy $\varnothing \neq T \subset S$, S is both *NF* and *UDS*, but T is neither *NF* nor *UDS*. This example, too, will be constructed from a preceding one by suitably adjoining a third player. Take $(X_1,X_2,\varrho_1,\varrho_2)$ as before, and take $X_3 = \{\alpha,\beta\}$; ϱ_3 is the numerical ">" relation. Following the model of the previous example, let

$$f_1(A,a,\alpha) = 1, f_1(B,a,\alpha) = 2, f_1(A,b,\alpha) = f_1(B,b,\alpha) = 0$$

and $f_2(x_1,x_2,\alpha) = -f_1(x_1,x_2,\alpha)$ for all $(x_1,x_2) \varepsilon X_1 \times X_2$. This is already enough to assure that $T = \{1,2\}$ is neither *NF* nor *UDS*. To make $S = \{1,2,3\}$ both *NF* and *UDS*, set

$$f_1(x_1,x_2,\beta) = 3 \text{ for all } (x_1,x_2) \varepsilon \mathrm{X}_1 \times \mathrm{X}_2,$$

$$f_2(x_1,a,\beta) = 3, f_2(x_1,b,\beta) = 4 \text{ for all } x_1 \varepsilon X_1,$$

$$f_3(x_1,x_2,\alpha) = 0 \text{ for all } (x_1,x_2) \varepsilon X_1 \times X_2,$$

$$f_3(x_1,a,\beta) = 0, f_3(x_1,b,\beta) = 1 \text{ for all } x_1 \varepsilon X_1.$$

An initial impression from these findings might be, that despite the motivating observation with which the present paper began, aggregability of a subset of the players does not really have much to do with the parallelism of those players' interests. I presently prefer an alternative interpretation, namely that the findings are corrective to an implicit assumption that parallelism of players' interests must (like parallelism of sets of lines in the Euclidean plane) be viewed as equivalence-derived from a binary relation of "parallel interests" between individual *pairs* of players. The formulation of a different concept of parallel interests for a subset of the players, and the study of the relationship between that concept and aggregability, are planned for a subsequent paper.

4. Approximations

Since the topics of this section deal with quantitative rather than qualitative relationships, we now take all sets R_i and T_j to be the set of real numbers, and take all the relations ϱ_i and τ_j to be the ordinary numerical "greater than" relation. Theorems 1 and 3 involve the notions of an equilibrium point, of an aggregation of a given game G, and of conditions *NF* and *UDS*. The definitions of these concepts involve elements of an essentially order-theoretic nature (the linear-order properties of ϱ_i and τ_j; the monotonicity of F_j). To obtain "approximate" versions of the theorems, it will be necessary to replace these "ordinal" elements by suitable "cardinal" ones. The particular replacements introduced below appear reasonable, but other plausible alternatives may be more appropriate in particular contexts.

For each $i \varepsilon \mathrm{N}$ and each $x \varepsilon \mathrm{X}$, the quantity

$$M_i(x) = \sup\{f_i(x,i,x_i) : x_i \varepsilon X_i\} - f_i(x)$$

is nonnegative. If $\delta = (\delta_1, \ldots, \delta_n)$ is an n-tuple of positive real numbers, and if $x^\circ \varepsilon X$ satisfies

$$M_i(x^\circ) \leqslant \delta_i \text{ (all } i \varepsilon N), \tag{9}$$

then x° will be called a δ-*EP* of game G. Approximate *EP*'s of $G[B,F]$ are defined similarly.

We will say that F_j is *(k_j^+,k_j^-)-bounded monotone* in each argument, where k_j^+ and k_j^- are positive constants, if for each $s_j \varepsilon S_j$, and for any $i \varepsilon B_j$ with r_i the i-th coordinate of s_j, and for any $r_i' \varepsilon R_i$,

$$r_i' > r_i \text{ implies } 0 < k_j^- \leqslant [F_j(s_j,i,r_i') - F_j(s_j)]/(r_i' - r_i) \leqslant k_j^+. \tag{10}$$

This hypothesis expresses the plausible idea that an aggregate player's payoff should respond "in a bounded manner" to changes in the payoffs of the individual players comprising the aggregate. Note that (10) holds with $k_j^+ = k_j^- = 1$ if $F_j(s_j)$ is the sum (as in [5]) of the coordinates of s_j.

For a given $c > 0$, a subset S of N will be called *$NF(c)$* if for all $x \varepsilon X$, if there is an $i \varepsilon S$ and an $x_i \varepsilon X_i$ such that $f_i(x,i,x_i) > f_i(x)$, then there is an $x_S \varepsilon X_S$ such that $f_k(x,S,x_S) \geqslant f_k(x)$ for all $k \varepsilon S$ and

$$f_k(x,S,x_S) - f_k(x) \geqslant c\,[f_i(x,i,x_i) - f_i(x)] \tag{11}$$

holds for at least one $k \varepsilon S$. (The intuitive interpretation of this condition follows readily from that given earlier for NF.)

THEOREM 6. *Assume* F_j *is* (k_j^+,k_j^-)*-bounded monotone and* B_j *is* $NF(c_j)$ *for all* $j \varepsilon M$. *Let* δ *be a positive* n*-tuple and* δ' *a positive* m*-tuple such that* $\delta_i \geqslant \delta'_{j(i)}/k_{j(i)}^- c_{j(i)}$ *for all* $i \varepsilon N$. *If* x° *is a* δ'-EP *for* $G[B,F]$, *then* x° *is also a* δ-EP *for* G.

PROOF. Suppose, to the contrary, that $f_i(x^\circ,i,x_i) - f_i(x^\circ) > \delta_i$ for some $i \varepsilon S$ and some $x_i \varepsilon X_i$. Let $j = j(i)$. Since B_j is $NF(c_j)$, there is a $y_j \varepsilon Y_j$ such that $f_k(x^\circ,j,y_j) \geqslant f_k(x^\circ)$ for all $k \varepsilon B_j$, with

$$f_k(x^\circ,j,y_j) - f_k(x^\circ) \geqslant c_j\,[f_i(x^\circ,i,x_i) - f_i(x^\circ)] > c_j \delta_i \tag{12}$$

holding for at least one $k \varepsilon B_j$. Consider changing the arguments of $F_j[\{f_k(x^\circ) : k \varepsilon B_j\}]$ one at a time to those of $F_j[\{f_k(x^\circ,j,y_j) : k \varepsilon B_j\}]$, beginning with a $k \varepsilon B_j$ for which (12) holds. It follows from (10) and the last display that

$$g_j(x^\circ,j,y_j) - g_j(x^\circ) > k_j^- c_j \delta_i,$$

yielding a contradiction to the assumption that x° is a δ'-EP for $G[B,F]$.

Theorem 6 is an "approximate" version of Theorem 1. To obtain an "approximate" version of Theorem 3, we first define subset S of N to be *$UDS(c)$*, where $c > 0$, if for all $x \varepsilon X$, if $f_k(x,S,x_S) > f_k(x)$ holds for some $k \varepsilon S$ and $x_S \varepsilon X_S$, then

$$f_i(x,i,x_i) - f_i(x) \geqslant c\,[f_k(x,S,x_S) - f_k(x)]$$

holds for some $i \varepsilon S$ and $x_i \varepsilon X_i$. (The intuitive interpretation follows from that given earlier for UDS.)

THEOREM 7. *Assume* F_j *is* (k_j^+,k_j^-)*-bounded monotone and* B_j *is* $UDS(c_j)$ *for all* $j \varepsilon M$. *Let* δ *be a positive* n*-tuple and* δ' *a positive* m*-tuple such that* $\delta_i \leqslant c_{j(i)}\delta'_{j(i)}/k_{j(i)}^+|B_{j(i)}|$ *for all* $i \varepsilon N$. *If* x° *is a* δ-EP *for* G, *then* x° *is also a* δ'-EP *for* $G[B,F]$.

PROOF. Suppose, to the contrary, that $g_j(x^\circ,j,y_j) - g_j(x^\circ) > \delta_j'$ for some $j \varepsilon M$ and $y_j \varepsilon Y_j$. Consider changing the arguments of $F_j[\{f_k(x^\circ) : k \varepsilon B_j\}]$ one at a time to those of $F_j[\{f_k(x^\circ,j,y_j) : k \varepsilon B_j\}]$; it follows from (10) that

$$\begin{aligned} g_j(x^\circ,j,y_j) - g_j(x^\circ) &\leqslant k_j^+ \Sigma\{\max[0, f_k(x^\circ,j,y_j) - f_k(x^\circ)] : k \varepsilon B_j\} \\ &\leqslant k_j^+ |B_j| \max\{f_k(x^\circ,j,y_j) - f_k(x^\circ) : k \varepsilon B_j\}. \end{aligned}$$

Thus there must be a $k\varepsilon B_j$ for which

$$f_k(x^\circ,j,y_j) - f_k(x^\circ) > \delta_j'/k_j^+|B_j|.$$

Since B_j is $UDS(c_j)$, it follows that there must be an $i\varepsilon B_j$ and an $x_i\varepsilon X_i$ such that

$$f_i(x^\circ,i,x_i) - f_i(x^\circ) > c_j\delta_j'/k_j^+|B_j|,$$

yielding a contradiction to the assumption that x° is a δ-EP for G.

Note that the presence of k_j^+ in (10) is required for Theorem 7 but not for Theorem 6, and *vice versa* for k_j^- (so long as F_j is assumed monotone). The two theorems are not intended to apply simultaneously to the same pair (δ,δ'). Theorem 6 directly generalizes Theorem 3 of [1], an extension of which is obtained by taking all $c_j=1$, all $k_j^+=k_j^-=1$, and each $F_j(s_j)$ to be the sum of the coordinates of s_j. Making the same choices in Theorem 7 yields a result closely related to Theorem 4 of [1].

5. References

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