

Precise Equilibrium Constants from Spectrophotometric Data: BrCl in Br₂/Cl₂ Gas Mixtures

Joel Tellinghuisen

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

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The equilibrium constant for the reaction, Br₂(g) + Cl₂(g) ⇌ BrCl(g), is estimated using the classic spectrophotometric method with precise data and a multispectrum fitting approach. Analysis of spectra for 18 Cl₂:Br₂ mixing ratios yields $K^\circ = 9.1$ at 22 °C, with a nominal statistical error (1 σ) of 0.04. This error translates into a remarkable precision of 0.4 cm⁻¹ in the dissociation energy of BrCl, easily beating that for the current best spectroscopic estimate (± 5 cm⁻¹). However, a sensitivity analysis shows that K° is susceptible to small systematic errors and minor changes in the least-squares fit model, leading to a more conservative estimate of 2% error. The derived K° is consistent with statistical mechanical estimates that employ the current value for the BrCl dissociation energy, but it differs considerably from some recently measured and used values, which range from 6.4 to 10.4. The revised estimate of the BrCl dissociation energy is $\mathcal{D}_e = 18\,248 \pm 2$ cm⁻¹.

Introduction

The diatomic interhalogens are formed readily in the gas phase reaction



In all cases, this reaction favors the product interhalogen, but the tendency is weakest for BrCl, where K° is only ~ 10 . Thus, appreciable amounts of Br₂ and/or Cl₂ are always present along with BrCl for any mixing ratio of the parent gases. Because all three species absorb light in the UV–visible spectral region, spectrophotometry has been the method of choice for determining K° and the absorption cross-section of BrCl(g). In a modern reexamination of this problem, Maric et al.¹ recorded spectra at a dozen different Cl₂:Br₂ mixing ratios, from 1:4 to 31:1, and obtained $K^\circ = 10.1 \pm 1.1$ at 25 °C. They also reviewed earlier work in detail and, noting that their K° value was the largest yet obtained, suggested that further work was desirable. At least two subsequent determinations have appeared, but they have hardly settled the issue: Cooper et al.² obtained 7.0 ± 0.3 and Bartlett and Margerum³ estimated 10.4 ± 0.4 . For reference, two widely used tabulations of thermodynamics data yield 6.86^4 and 7.69^5 for K° at 25 °C.

Recently, I pointed out that the accuracy and precision of K° are limited by a single uncertain spectroscopic parameter, the dissociation energy of BrCl.⁶ Using the most recent assessment of this quantity ($\mathcal{D}_e = 18\,247 \pm 5$ cm⁻¹),⁷ from analysis of predissociation data⁸ for $v = 6$ in the *B* state of BrCl, I obtained $K^\circ = 8.9_5 \pm 0.5$. The 6% uncertainty in K° comes entirely from the uncertainty in \mathcal{D}_e , which resulted from the need to estimate a large centrifugal barrier in the predissociating state. Other predissociation data, for $v' = 7$,^{8,9} limit \mathcal{D}_e to a maximum value of $18\,253$ cm⁻¹ and K° to values < 9.6 .

While the spectroscopic data might seem to settle this issue, there are reasons why further pursuit of the spectrophotometric approach is worthwhile: (i) The determination of \mathcal{D}_e in ref 7 rested on the assumption that the predissociating state was the ¹Π analogue of the states responsible for spontaneous predissociation in I₂ and Br₂,¹⁰ while this is highly likely, it is not certain. (ii) A preliminary attempt to reanalyze the data of Maric et al.¹ by a multispectrum fitting method suggested that such an approach should be capable of yielding K° with a precision better than 1%.¹¹ This corresponds to an uncertainty of < 1 cm⁻¹ in \mathcal{D}_e , which rivals direct spectroscopic methods and constitutes a remarkable testament to the power of modern data analysis methods in what is essentially a thermochemical determination. (iii) At the same time, the least-squares (LS) analysis was highly sensitive to small changes in assumptions, including changes in the weighting algorithm for the different spectra. If the full potential of such an approach is to be realized, a better understanding of the role of systematic errors is desirable.

The present study was undertaken to address these issues. Absorption spectra of Cl₂/Br₂ gas mixtures have been recorded with high precision at room temperature, over the spectral region of 190–650 nm. The data have been analyzed by a nonlinear LS multispectrum fitting model, which has been varied extensively in trial-and-error fashion to examine the model error. The results support the statistical mechanical estimate of K° , confirm the great potential precision of the method, and characterize quantitatively the sensitivity to a number of possible systematic errors.

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Experiment Section

Absorption spectra of Cl₂, Br₂, and mixtures of the two ranging from 8:1 to 1:3 Cl₂:Br₂ were recorded at a resolution and interval of 1 nm on a Shimadzu UV-2101PC UV–visible spectrophotometer, using a 1.0 cm quartz cuvette and a 9.71 cm (± 0.01 cm) quartz cell equipped with Suprasil windows. No check was made of the photometric accuracy, which is stated as ± 0.004 at $A = 1$ by the manufacturer. The cells were attached to a vacuum line (~ 1 mTorr minimum pressure—1 Torr ≈ 133 Pa) for direct pressure measurement with a quartz bourdon gauge (Texas Instruments), which was calibrated against a mercury manometer. The sensitivity and precision of the pressure measurements was ~ 0.01 Torr, and the absolute accuracy (from the calibration) was estimated to be $\sim 0.1\%$ for $P > 10$ Torr.

TABLE 1: Cl₂/Br₂ Mixtures and Pressures for Recorded Spectra

no. ^a	r ^b	P range (Torr) ^c	no. ^a	r ^b	P range (Torr) ^c
1	2.194	111	10	1.174	112
2	1.472	48–127	11	0.4124	73
3	0.619	74	12	1.0021	98
4	8.27	140	13	2.23	120
5	3.32	133	14	2.23	15–39
6	0.369	59–72	15	1.0014	27
7	5.377	72–155	16	0.4645	14
8	1.784	106	17	4.033	25–32
9	0.4679	61	18	0.3355	21–32

^a 1.0 cm cuvette used for 1–13; 9.71 cm cell used for 14–18.
^b Mixing ratio, [Cl₂]₀/[Br₂]₀. ^c 1.00 Torr ≈ 1/750 bar.

The experiments were conducted at room temperature (22.0 ± 0.5 °C). Although subsequent (static) checks showed that the instrument's cell compartment could warm by as much as 3 °C over the course of a day, the consistency among the data themselves in the LS analysis was ~0.3%, indicating that temperature variations were limited to 1 °C.

Bromine (Fisher, reagent grade) was stored in a bulb on the vacuum system following trap-to-trap distillation at 0 °C and differential evaporation designed to minimize the more volatile (Cl₂) and less volatile (water) impurities. Chlorine (Matheson, high purity) was admitted to the system directly from a lecture bottle. Spectra of both pure gases were taken on a number of days, for both the short and the long path length cells. The system was always rinsed with at least one portion of each pure gas prior to its use for obtaining these spectra. A similar procedure was used to prepare the mixtures, in the course of which the spectrum of the Cl₂ was normally taken as a check against possible contamination with residual Br₂.

The relevant volumes of the vacuum system were calibrated using air at low pressures. The ideal gas law was used at all times in these calibrations and in converting pressures to concentrations for the analysis of the absorption data.

The mixtures were prepared by using liquid nitrogen to freeze measured pressures of each gas together in a mixing bulb. The mixtures were then exposed to light and heat from a quartz halogen lamp for at least 10 min to facilitate mixing and equilibration. After it was cooled back to room temperature, each mixture was first expanded into the main vacuum manifold and then after several minutes, into the absorption cell. Spectra were recorded after a further wait of several minutes for thermal and pressure stabilization. Then, the mix was recondensed in the mixing bulb and the procedure was repeated at least once. In this way, spectra were obtained 2–4 times for each mixture, often at two or more total pressures, and typically over a total time period of 3 h. There was never any indication from these multiple spectra that chemical equilibration was incomplete: The greatest disparity observed in the estimated molar absorptivity for a single mixture was 0.8% and was essentially constant across the spectrum. The estimated absorptivity ϵ_λ was usually taken as a simple average of the several spectra for a given mix, although in a few cases outlier spectra were excluded. Results were obtained for 13 mixtures in the short cell and five in the long, as summarized in Table 1.

The spectra recorded using the 1 cm cuvette involved mixtures at typical pressures of ~100 Torr and yielded peak absorbances of ~0.5. Pressures a factor of five lower were used for the 10 cm cell, yielding peak $A \approx 1$. Because of the expansion methods used, the initial pressures in the mixing bulb were a factor of five larger. After the gas was expanded into the manifold, the pressure typically declined by ~0.2 Torr per

minute initially. On further expansion into the cuvette (which involved another 20% drop in P), the rate of decline dropped sharply. This behavior is tentatively attributed to adsorption of the gas on the walls of the system (including the bourdon gage). Similar behavior was observed for pure Br₂ but not for Cl₂, and it seemed stronger for the Br-rich mixtures. Thus, it is possible that this adsorption involves Br₂ (and perhaps BrCl) preferentially, which makes it a potential source of systematic error. The effect on the mixing ratios is at most ~1%; however, the LS analysis fails to substantiate this problem (see below).

Absorption spectra of gases at low P deviate negatively from Beer's law in regions of discrete (line) absorption. For the present study, the main problem in this respect is the Br₂ absorption, which shows such deviations for $\lambda > 510$ nm.¹² For the determination of the equilibrium constant K° , only data for $\lambda < 510$ nm were used. To obtain reliable low-resolution spectra for BrCl in the region $\lambda > 510$ nm, spectra of Br₂ and of several of the mixtures were recorded with admixture of ~700 Torr N₂, using the long path cell (where the halogen concentrations were low).

Spectral Fitting Method. Because reaction 1 conserves molecules, the molar absorptivity ϵ_λ for any mixture can be obtained as a function of wavelength from the measured absorbance A_λ using the Beer's law definition, $A_\lambda = \epsilon_\lambda c l$, where c is the concentration and l is the path length. The absorbance is the usual base 10 logarithm of the reciprocal transmittance, $A = \log(I_0/I)$. For any mixture at any wavelength, the absorptivity of the mix can be represented as a weighted average of the contributions from the three species:

$$\epsilon_\lambda(\text{mix}) = f_{\text{Br}_2} \epsilon_\lambda(\text{Br}_2) + f_{\text{Cl}_2} \epsilon_\lambda(\text{Cl}_2) + f_{\text{BrCl}} \epsilon_\lambda(\text{BrCl}) \quad (2)$$

The equilibrium fractions f_i of the three components are related to the initial mixing ratio, $r = [\text{Cl}_2]_0/[\text{Br}_2]_0$, through the equilibrium constant K° :

$$f_{\text{BrCl}} = Y(1 - Z^{1/2}) \quad (3)$$

where $Y \equiv K^\circ/(K^\circ - 4)$ and $Z \equiv 1 - (4/Y)r(1 + r)^{-2}$. The other fractions are then

$$f_{\text{Br}_2} = (1 + r)^{-1} - f_{\text{BrCl}}/2 \quad (4)$$

and $f_{\text{Cl}_2} = 1 - f_{\text{BrCl}} - f_{\text{Br}_2}$. Through these relations, all of the mixture spectra contain information about K° and the spectra of all three components.

The LS model developed to analyze the data contained no assumptions beyond these. In addition, I measured the absorption for the pure parent gases under the same conditions as used for the mixtures and treated $\epsilon_\lambda(\text{Br}_2)$ and $\epsilon_\lambda(\text{Cl}_2)$ as known (although uncertain in some computations). Thus, the fit model processed the spectral data for all mixtures (or specified subsets) in terms of a single K° and a single value of $\epsilon(\text{BrCl})$ at each wavelength. The data were typically analyzed in this fashion for every third to fifth λ value, over a specified λ range, giving K° and 50–90 $\epsilon_\lambda(\text{BrCl})$ values for up to 1600 total ϵ_λ values.

The precision of spectrophotometric data depends inherently on the specific instrument and on the wavelength and strength of the absorption. To assign weights to the data, I started with a statistical error calibration for the Shimadzu instrument¹³ and added a percentage uncertainty for each spectrum, with the latter based on observations from the multiple spectra for a given mix. The scaled contribution was taken to be 0.3–0.4% in different calculations; this exceeded the instrumental value except for very weak absorption, so the statistical error at each wavelength

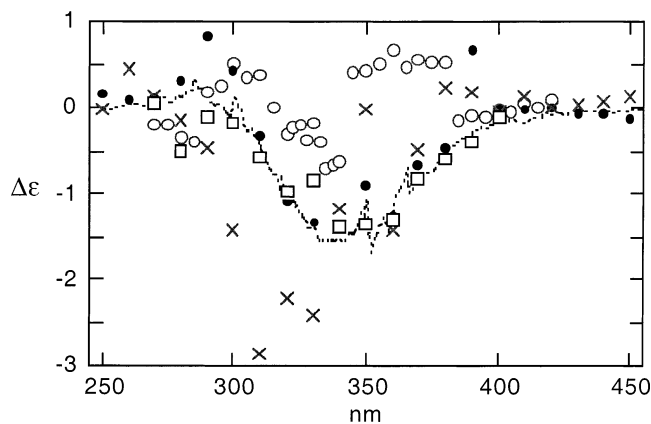


Figure 1. Differences (other, this work) in molar absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$) of $\text{Cl}_2(\text{g})$ at room temperature, from Seery and Britton (●),¹⁷ Burkholder and Bair (○),¹⁸ Hubinger and Nee (×),¹⁹ Ganske et al. (□),²⁰ and Maric et al. (dashed).²¹ From the present work, the peak absorptivity at 22 °C is $68.3 \text{ L mol}^{-1} \text{cm}^{-1}$ at 330 nm, and the standard error near the peak (from an average of 10 spectra) is $0.12 \text{ L mol}^{-1} \text{cm}^{-1}$.

was taken as a combination of the $A = 0$ instrumental value (converted to ϵ) and the percentage error. Weights were then defined in the usual way, as $w_i = \sigma_{\lambda_i}^{-2}$. A percentage error of 0.4% yielded reduced χ^2 values near unity for the fits, supporting the reasonability of this assessment.¹⁴

The nonlinear fit algorithm employed fairly standard methods,^{14–16} with all partial derivatives obtained numerically, by finite difference, using part in 10^5 changes in the parameters.

Results and Discussion

Experimental Spectra. Reliable spectra for the pure parent gases are essential, so ϵ_λ was obtained for each parent gas by averaging 5–10 spectra recorded at different pressures, in both absorption cells. On most days, further checks were made of the pure gases to guard against contamination in the preparation of the mixtures. These checks nearly always agreed with the reference spectra within $\sim 0.3\%$ at peak absorption (330 nm for Cl_2 , 416 nm for Br_2).

Results for Cl_2 are compared with other determinations in Figure 1. The present values agree most closely with the spectra of Burkholder and Bair¹⁸ but still deviate in some regions by as much as 0.7%. Differences are larger and more systematic in the comparisons with other results and are greatest for the most recently published results from Hubinger and Nee.¹⁹ From the standpoint of the present analysis, the differences are quite significant in the region of strongest absorption. For example, two different determinations two years apart, each involving an average of eight or more spectra, agreed in peak absorptivity within $0.1 \text{ L mol}^{-1} \text{cm}^{-1}$, and the weakest single spectrum (deemed an outlier) recorded for either the short or the long path cell was only $1 \text{ L mol}^{-1} \text{cm}^{-1}$ weaker near the peak.

The Br_2 spectra recorded on this system were compared previously with other results, in conjunction with a quantum reanalysis of the absorption transitions in this molecule.¹² However, the Br_2 spectra obtained using the long cell at low pressures in the present work are weaker by $\sim 1\%$ than those recorded at higher pressures in the short cuvette, an effect that I have attributed mainly to possible path length errors for the 1 cm cuvette and deviations from ideal gas behavior²² at the relatively high P_s involved (29–107 Torr). A reanalysis of the absorption data in ref 12 with inclusion of a scaling parameter for my spectra yields a better fit and a value of 0.9937(6) for this parameter,²³ which mainly just adjusts my spectra into optimal agreement with the older data of Passchier et al.²⁴ The

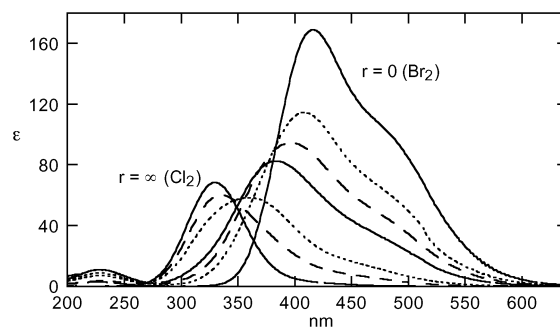


Figure 2. Absorption spectra (molar absorptivity) for Cl_2 , Br_2 , and several Cl_2/Br_2 mixtures at 22 °C. From top to bottom at 400 nm, the spectra are for pure Br_2 (indicated), $r = 0.336, 0.619, 1.00, 3.32, 8.27$, and ∞ (Cl_2 , indicated).

adjusted peak absorptivity is $170.1 \text{ L mol}^{-1} \text{cm}^{-1}$. The spectra of Cl_2 and Br_2 are illustrated in Figure 2, along with representative spectra for the mixtures.

LS Analysis. Because of concerns about the reliability of the Cl_2 and Br_2 spectra, their transferability from long to short path spectra, the possibility of preferential adsorption of Br_2 on the walls of the vacuum system, temperature and path length uncertainties, and proper weighting of the various spectra, considerable trial-and-error LS fitting was carried out on the data. In course, the LS model was altered to incorporate correction factors (i) to scale the Br_2 and/or Cl_2 spectra, for either or both of the cells, (ii) to scale the mixture spectra for either the short or the long path cell, and (iii) to adjust the mixing ratio for selected spectra or for all spectra. Further, the weighting algorithm was varied, and the effects of selective deletion of data subsets and wavelength ranges were examined. The primary results of these computations may be summarized as follows:

(i) With all data in the range of 250–510 nm included in the fit, the nominal precision (1σ) of K° is 0.04, which corresponds to a remarkably small uncertainty of 0.4 cm^{-1} in \mathcal{D}_e for BrCl.

(ii) However, the results are highly sensitive to small systematic errors of the type mentioned, so that it is difficult to realize this precision. My best estimate of K° is 9.1 ± 0.2 . This value is consistent with the spectroscopy/statistical mechanical-based estimate and is more precise by a factor 2.5, corresponding to an uncertainty of 2 cm^{-1} in \mathcal{D}_e for BrCl.

Of all the possible correction parameters discussed above, one was clearly indicated and was incorporated in the final fitting: a scale factor for all of the measured ϵ_λ values obtained with the 1 cm cuvette. The actual value varied slightly depending on the wavelength range included in the analysis, but a typical value was 0.9934(4). This is close to the previously mentioned correction factor for the Br_2 spectra obtained with this same cuvette, suggesting that it is largely a path length adjustment. Without this correction, the fit χ^2 was 38% larger, and K° was smaller by 0.25.

At the Br_2 pressures used in many of the mixtures, ϵ_λ for Br_2 is P -dependent below 250 nm, due to formation of dimers.²² Thus, the fitting was restricted to $\lambda > 250 \text{ nm}$. As was already noted, the maximum wavelength was taken as 510 nm. In one of the sensitivity tests, data were fitted in the range $\lambda_s - 510 \text{ nm}$. As λ_s was increased from 250 to 360 nm, K° dropped by 1%.

Other factors examined in the sensitivity analysis had similar effects on the LS value of K° . Selective deletion of individual data sets increased or decreased K° by as much as 1%. Reasonable changes in the weighting algorithm had a comparable impact. These included varying the proportional error factor from its final value of 0.004, increasing and decreasing

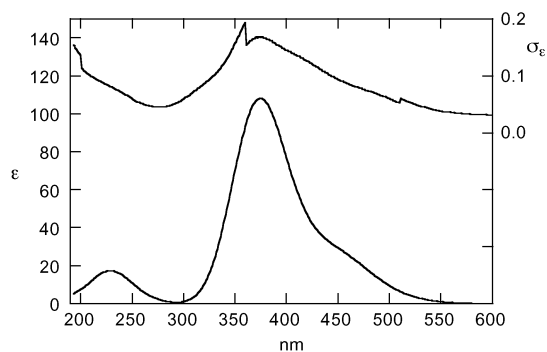


Figure 3. Derived spectrum (molar absorptivity, $\text{L mol}^{-1} \text{cm}^{-1}$) of BrCl at 22 °C and statistical error (top, scale to right).

the base ($\epsilon = 0$) uncertainty, and treating the Br_2 and Cl_2 spectra and the r values as statistically uncertain.

The correction parameter that yielded the greatest change in K° was the hypothetical Br_2 adsorption adjustment. This was taken as a single scale factor for all of the r values, and although it differed only slightly from unity [0.9920(12)], including it reduced the χ^2 of the fit by over 4% and increased K° by 3%. Although it seems likely that some such effects did occur in the experiments, the justification for this correction is less clear-cut than that for the 1 cm data, especially since the direction is wrong for preferential adsorption of Br_2 . It is conceivable that this parameter is compensating for some other systematic effect in the preparation of the mixtures. In partial deference to it, I have adjusted my final recommended value for K° upward from 9.0 to 9.1. The uncertainty of 2% loosely encompasses the larger value of K° that is obtained when this parameter is included in the model.

The value of $K^\circ = 9.1$ at 22 °C corresponds to 9.0₃ at 25 °C. This is consistent with the statistical mechanical value, and it implies a dissociation energy for BrCl, $\mathcal{D}_e = 18\,248(2) \text{ cm}^{-1}$.

BrCl Spectra. The low-resolution molar absorptivity of BrCl obtained from this analysis is illustrated together with its statistical error in Figure 3. For the region 250–510 nm, these spectra were obtained directly from the LS fit, with $K^\circ = 9.1$; and the displayed error in Figure 3 is the directly obtained statistical error. The regions $\lambda < 250 \text{ nm}$ and $\lambda > 510 \text{ nm}$ were obtained from a smaller data set of seven spectra all having large r (hence small P_{Br_2}). These results were compared with those from a smaller data set involving only the lower P spectra from the 9.7 cm cell and found to be consistent. Also, comparisons of pressurized and unpressurized spectra for these Cl_2 -rich mixtures showed no significant differences for $\lambda > 510 \text{ nm}$. A pressurized Br_2 spectrum was used in the analysis.

The plotted statistical error in Figure 3 ignores the possible systematic effects. However, a 1% change in K° alters ϵ_λ by at most $0.12 \text{ L mol}^{-1} \text{cm}^{-1}$, which amounts to only 0.1% change in ϵ_λ near the main peak. Incorporation of the r scaling factor in the analysis has a comparable impact, for each percent change in K° .

The present BrCl spectrum is compared with other determinations in Figure 4. The new spectrum agrees most closely with that of Maric et al.,¹ except in the vicinity of the strongest peak (Figure 4B), where it agrees better with the early determination of Seery and Britton.

A significant contribution to the BrCl absorption in the main peak comes from the $B \leftarrow X$ transition, which is also responsible for discrete absorption in other halogens.^{8–10,25} The role of other transitions in the spectrum has been the topic of several recent studies^{1,2,19,26,27} but is not a primary concern in the present work and so will not be considered further.

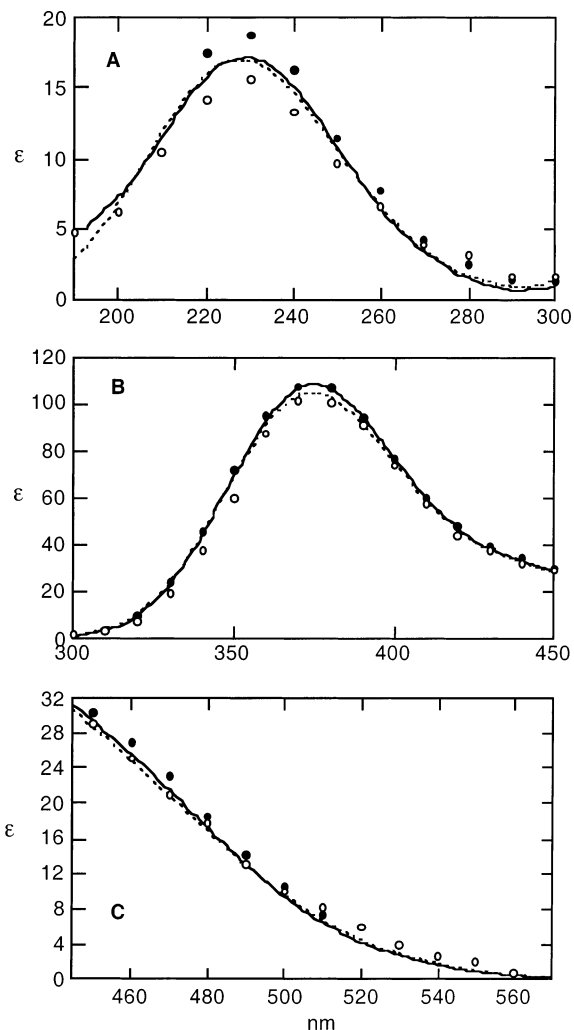


Figure 4. Comparison of present BrCl spectrum with other determinations: Seery and Britton (●),¹⁷ Hubinger and Nee (○),¹⁹ and Maric et al. (dashed).¹

The experimentally measured and derived spectra for Cl_2 and BrCl are presented at 10 nm intervals in Table 2. Cubic spline fits to these spectra reproduce the omitted values (at 1 nm intervals) with rms and maximum errors of 0.06 and 0.3 $\text{L mol}^{-1} \text{cm}^{-1}$, respectively.

Conclusion

The equilibrium constant for the formation of BrCl(g) from $\text{Cl}_2(\text{g}) + \text{Br}_2(\text{g})$ has been estimated from a multispectrum nonlinear LS analysis of spectrophotometric data. A fit of spectra for 18 different mixing ratios of Cl_2 and Br_2 yields K° with a remarkable statistical precision of 0.4%, which translates into an uncertainty for the dissociation energy of BrCl that is an order of magnitude smaller than the current $\pm 5 \text{ cm}^{-1}$ from spectroscopic data. However, the LS analysis is quite sensitive to possible systematic errors in the data and to minor changes in the fit model, including assumptions about the weights of the data and the wavelength region chosen for analysis. The estimate of K° is particularly sensitive to systematic errors in the mixing ratio: A decrease by 0.8% for all r values led to a 3% increase in K° .

The K° value from this study is in complete accord with the statistical mechanical estimate, which relied upon an interpretation of predissociation data for the BrCl dissociation energy. This interpretation involved the assumption that the predisso-

TABLE 2: Experimental Spectra for Gaseous Cl₂ and BrCl at 22 °C

λ (nm) ^a	λ_{cor} (nm) ^b	ϵ_{λ} (Cl ₂) ^c	ϵ_{λ} (BrCl) ^c	λ (nm) ^a	λ_{cor} (nm) ^b	ϵ_{λ} (Cl ₂) ^c	ϵ_{λ} (BrCl) ^c
200	200.14	0.17	7.28	410	410.06	3.49	59.99
210	210.07	0.05	11.58	420	420.15	2.61	46.95
220	220.13	0.04	15.59	430	430.08	1.98	38.59
230	230.08	0.06	17.15	440	440.14	1.49	33.28
240	240.13	0.04	15.01	450	450.09	1.05	29.40
250	250.07	0.12	10.73	460	460.15	0.73	25.61
260	260.14	0.60	6.47	470	470.09	0.47	21.59
270	270.06	2.22	3.33	480	480.16	0.30	17.25
280	280.14	6.88	1.46	490	490.08	0.20	13.18
290	290.05	16.39	0.70	500	500.17	0.12	9.46
300	300.14	31.28	1.01	510	510.09	0.07	6.53
310	310.06	48.80	3.48	520	520.18	0.03	4.32
320	320.13	63.10	10.13	530	530.10	0.04	2.75
330	330.07	68.32	23.26	540	540.18	0.01	1.72
340	340.13	62.98	44.45	550	550.12	0.03	1.01
350	350.07	50.41	69.82	560	560.18	0.03	0.57
360	360.13	35.38	93.09	570	570.13	0.03	0.33
370	370.06	22.45	106.37	580	580.19	0.03	0.20
380	380.14	13.32	106.06	590	590.13	0.02	0.14
390	390.06	7.95	94.32	600	600.21	0.02	0.09
400	400.15	5.04	76.85				

^a Fiducial wavelength. ^b Corrected standard air wavelength, from ref 13. ^c Molar absorptivity, units L mol⁻¹ cm⁻¹.

ciating state was the same C¹Π state that is responsible for spontaneous predissociation in I₂ and Br₂. While this attribution seemed highly likely, the present agreement provides corroboration.

There is little doubt that K^o values derived from experimental spectrophotometric data should agree with the ideal gas values from statistical mechanics. It is true that the current measurements for the 1 cm cuvette involved higher pressures than have been used in such experiments in the past. At the highest Br₂ pressures (60 Torr), ideal gas deviations for this species are almost 0.4%, and absorption by Br₂ dimers below 250 nm is evident.²² However, there was no indication, from residuals analysis, of absorption by any species other than Cl₂, Br₂, and BrCl in the 250–510 nm region employed for the analysis. This result is consistent with more extensive checks for deviation from Beer's law by others.¹ The LS reduced χ^2 of ~ 1 for the assumed 0.4% uncertainty in the mixture spectra confirms that this is a reasonable assessment of the uncertainties associated with temperature and mixture preparation in the present study.

The halogen spectra under investigation here have become of importance to atmospheric modeling in recent years.^{1,21,28} While the differences between the present absorptivities and those recommended in ref 28 are not likely to be significant in such applications, it is still surprising that recent estimates of ϵ_{λ} for a continuous absorption band in a molecule as simple as Cl₂ vary by >1% near the peak (Figure 1). Variations in the

estimates for BrCl are more understandable, since these are tied to the determination of K^o. In this regard, it should be noted that the BrCl absorption cross-sections presented in Table 56 of ref 28 are not computed from the recommended equation (from ref 1) but are the measured values from ref 19, which are arguably in poorest accord with other determinations.

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