

TOTAL EMISSIVITY OF HOT WATER VAPOR—I. HIGH PRESSURE LIMIT*

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Abstract—Recent measurements of the infrared spectral emissivity of hot water vapor at temperatures between 1000°K and 2250°K are used to determine the total emissivity of H₂O. In this work the total emissivity is determined (1) exactly for the experimental conditions at which the measurements were made and (2) in an approximation which provides an upper limit to the emissivity for optical depths other than those of the measurements. The first determination yields results which agree quite well with the values of total emissivity given at the same conditions by Hottel. The upper-limit values of the second determination are expected to be approached by the true emissivity at high temperatures and pressures. Some brief comparisons are presented with other predictions of the total emissivity of water vapor under these conditions.

NOMENCLATURE

- a , statistical band model parameter (ratio of line width to line spacing);
 \bar{a} , value of a averaged over an entire band;
 c_w , Hottel's correction factor to extend his chart to conditions other than $p_e \rightarrow 0$;
 k , absorption coefficient ($\text{cm}^{-1} \text{atm}^{-1}$);
 \bar{k} , absorption coefficient frequency—averaged over a small wavenumber interval;
 \bar{k}_{app} , apparent value of \bar{k} obtained by applying the statistical band model using \bar{a} ;
 \bar{k}_w , value of \bar{k} in the wing region of a band;
 l , path length (cm);
 N , spectral radiance ($\text{watts/cm}^2\text{-steradian-cm}^{-1}$);
 N_v^0 , blackbody spectral radiance;
 p , pressure (atm);
 p_e , partial pressure of emitting species;
 p_i , partial pressure of i th species;
 T , temperature (°K);

- u , standardized optical depth (cm atm)_{STP};
 Z , apparent absorption coefficient obtained directly from spectral emissivity data.

Greek symbols

- α_i , integrated intensity of the i th band ($\text{cm}^{-2} \text{atm}^{-1}$);
 ϵ , spectral emissivity;
 ϵ_T , total emissivity;
 ν , wavenumber (cm^{-1});
 $\nu_{c, i}$, wavenumber at the center of the i th band;
 ν_w , wavenumber at the band wing (low point between two bands);
 σ , Stefan-Boltzmann constant ($5.75 \times 10^{-12} \text{ W/cm}^2 \text{ degK}^4$).

INTRODUCTION

MANY PROBLEMS in heat transfer require specification of the radiant energy transferred from a hot gas to a nearby surface. Hot water vapor is a particularly important emission source, because it is present in the combustion products of most common fuels. If the gas is homogeneous, the radiative transfer problem can be formulated

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in terms of the total directional emissivity of a column of hot gas, or alternatively of the total emissivity of a hemispherical gas volume to an element of surface at its center. The total emissivity of a gas is a complicated function of the temperature, pressure, and composition of the gas, and of the pathlength along the line of sight.

The total emissivity of hot water vapor has been the subject of many previous investigations. The work up to about 1945 has been correlated and summarized by Hottel [1], whose presentation in chart form of his own data and those of other investigators has long been recognized as giving the "standard values" of hot water emissivity. The measurements from which these charts were performed were made at pressures near one atm, over quite a wide range of gas composition, and at optical depth and temperature conditions shown in Fig. 1. The chart also

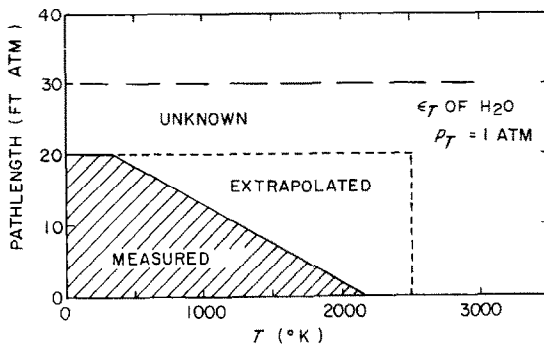


FIG. 1. Temperatures and optical depths for which reliable measurements of the total emissivities of H_2O vapor exist (pressures near 1.0 atm).

Here we have simply indicated the region for which the chart on p. 85 of [1] shows solid lines for ϵ_w ; the dotted lines on that chart are extrapolated values.

shows estimates of the water emissivity at other conditions where no data were available. Hottel cautions his readers that the values given in his charts are uncertain outside the range of the measurements, and particularly at pressures other than atmospheric. More recently Edwards *et al.* [2] have presented correlations of various experimental determinations of the

band absorptances of H_2O at temperatures between 300° and $1100^\circ K$ and equivalent pressures between 0.01 and 10 atm, where the equivalent pressure is taken as $P_{\text{eff}} = P_{N_2} + 5 P_{H_2O}$. The results are presented in terms of a wide-band adaptation of the Mayer-Goody statistical [3, 4] band model using a mean line-width to line-spacing ratio and spectral band contours calculated in the just-overlapping line model by Gray [5]. Edwards *et al.* give prescriptions from which emission may be calculated from isothermal or non-isothermal gas volumes. The measured band absorptances show mean deviations within 11 to 34 per cent from the correlation.

Penner and Thomson [6] have correlated the total emissivities presented by Hottel in two approximations. The first employed a "box" model for the different emission bands and the Mayer-Goody model to describe the effects of pressure and composition. The integrated intensities of the various bands (essentially unknown at the time of the calculations) were adjusted within reasonable limits to allow a best fit to Hottel's charts. It was hoped that the expression in terms of fundamental spectroscopic parameters would allow a reasonable extrapolation to other conditions than those measured. A second correlation was made in terms of a just-overlapping line calculation and an "effective" band width. Again, a fit to the experimental data was employed to evaluate the unknown parameters. At large optical depths, use of a "box model" or an "effective bandwidth" can lead to an underestimate of the contributions to ϵ_T from spectral windows, where recent measurements show emission to occur at high temperatures. Furthermore, the integrated band intensities derived from the curve-fits tend to be considerably lower than recently measured values; under conditions (lower optical depths) where emission is sensitive to band intensities, the predicted emissivities are also expected to be low. For these reasons, a re-examination of certain aspects of the H_2O emissivity, using realistic spectral band contours, is timely. Such

investigations have been undertaken by Penner, among others.

Penner and Varanasi [7] have presented a calculation of water emissivities based on recent measurements of the integrated intensities of the water bands. A simplified spectral band contour, still more realistic than the box model, was employed and a calculation equivalent to the just overlapping line model used. These authors suggested that the model should be applicable to pure water vapor at pressures above some value near one atm. They also accounted for Hottel's correlation of the effect of gas composition by assuming a model with randomly distributed dispersion lines. The first part of the Penner-Varanasi calculation is extensible to high temperatures.

For the past several years, a study of hot water vapor has been carried on in the authors' laboratory. Measurements of the spectral emissivities of H₂O have been made in a specially constructed flow apparatus. The purpose of this paper is to report certain features of the total emissivity which can be determined from these measurements, which were made at low optical depths. These include an integration of the spectral measurements to determine total emissivities which are compared with Hottel's data, determination of an accurate extrapolation of Hottel's data to very low pathlengths, and determination of total emissivities at high pressures which also represent an upper limit to the total emissivity at low pressures. This last result is similar in scope to the first Penner-Varanasi calculation, but is approached from a somewhat different point of view. The results which we report in this paper may be of use in the design of large furnaces, rocket combustion chambers, and other systems where H₂O vapor is present at high temperatures and either high pressures or long optical paths. They also show, to a reasonably good approximation, the relative contribution of the various regions of the spectrum to emission from hot water under various conditions, and are useful as a guide to further investigations. In a subsequent paper, we

shall indicate the effects of total pressure on the emissivity.

We should emphasize that it is not our purpose in this paper to "replace" existing measurements and correlations of the total emissivity of hot water vapor, but to examine the limiting values which the emissivity attains under certain conditions. Our point of view is that an accurate upper limit to a quantity is often as desirable as a "best estimate", and represents desirable information. The upper limit values which we present here are believed to be reliable when properly used. They are not needed for conditions where accurate measurements of ϵ_T exist, but should be useful where no data are available. We do not concern ourselves with the manner in which these are approached as the pressure is raised, but only with the ultimate asymptotic results. We are specifically concerned with high temperatures, where measurements at large optical depths have not been made at the time this paper is written.

THEORETICAL DEVELOPMENT

The rate of emission of radiant energy by a gas at uniform temperature and pressure into a small element of solid angle, $\delta\omega$, may in principle be expressed as

$$N_v(T, p, p_i, l) \delta\omega = \int_0^{\infty} N_v^0(T) \{1 - \exp[-k(v, T, p, p_i) p_e l]\} dv \delta\omega. \quad (1)$$

Here N is the emitted radiance in watts/cm²-steradian, N_v^0 is the Planck blackbody spectral radiance, k is the spectral absorption coefficient of the gas (a function of wavenumber v , temperature T , total pressure p , and partial pressure p_i of the species present in the gas mixture), p_e is the partial pressure of the emitting species, and l is the distance through the gas along the direction defined by $\delta\omega$. The total emissivity of the gas is

$$\epsilon_T(T, p, p_i, l) = 1/\sigma T^4 \int_0^{\infty} N_v^0(T) \{1 - \exp[-k(v, T, p, p_i) p_e l]\} dv. \quad (2)$$

The quantity in braces is the spectral emissivity of the gas.

If the absorption coefficient is a sufficiently slowly varying function of wavenumber, then it can be determined directly from measurements of the spectral emissivity of a gas at given conditions with a spectrometer of moderately good resolution. Equation (2) may then be used to calculate the total emissivity at all pathlengths with a reasonable amount of effort. Unfortunately, gaseous emitters such as H_2O and CO_2 exhibit emission spectra which vary extremely rapidly with wavenumber when viewed with spectrometers of very high resolution. The emission occurs in a very large number of discrete spectral lines, and the absorption coefficient varies by a large amount within the spectral band pass of all but the highest-resolution instruments. The amount of labor required to obtain absorption coefficients and to perform the integration over all significant wavenumbers would be prohibitive, if one went about things in a meticulous fashion, even with the aid of automated equipment and large computing machines.

Most measurements of gaseous spectral emissivities are therefore made with instruments of only moderate resolving power. These measurements do not show the fine structure of the emission spectrum. Because of this behavior, one cannot determine "true" absorption coefficients from the data presented by most investigators. One obtains instead a quantity which is related to the spectral absorption coefficient averaged over the spectral slit width of the measuring instrument. If one uses this quantity in equation (2) to obtain the spectral or total emissivity at pathlengths other than those observed, one will in general obtain values which are greater than the true values at longer paths and less than the true values at short paths.

If the observed gas is optically thin, such that $(kp_e l)$ is much less than one, then the spectral emissivity is a linear function of pathlength. Under these conditions, the quantity derived

from spectral emissivity measurements is the wavenumber-averaged absorption coefficient. The wavenumber-averaged absorption coefficient may also be obtained from experimental spectra obtained under conditions where fine structure effects are small. Extrapolations to pathlengths greater than those observed provide an upper limit to the spectral and total emissivity.

This upper limit to the emissivity is approached under either of two conditions. The first condition is that the pressure be high enough so that the line broadening effects produced by molecular collisions result in spectral lines whose widths are large compared to the average distance between lines. The line strength, which is a measure of the rate at which energy is emitted by a line, is essentially unaffected by pressure. As a result, the same amount of energy is emitted within a wide spectral interval, but the distribution over wavenumber is smooth and rather slowly varying as compared to the low-pressure distribution. As the pathlength increases, the centers of strong lines no longer tend to saturate long before other portions of the spectrum close by. The total emissivity therefore will approach that calculated by equation (2) using wavenumber-averaged absorption coefficients which likewise do not exhibit partial saturation over small intervals. The second condition is that the temperature be high enough so that a large number of vibrational and rotational energy states are populated. Spectral lines involving these states are closely spaced and overlap to some degree even at low pressures. As a result, the emission spectrum of the gas is a less rapidly varying function of wavenumber than at low temperatures, and the spectral emissivity approaches the calculated upper limit at pressures lower than those required at low temperatures.

A word of caution should be added here as to the conditions under which these upper-limit calculations are absolute. As the pressure continues to increase to very high values, a strong spectral line near the center of the band may become so broad that its "tail" is stronger at the edges of the band than are the centers of

weak lines centered at the band wings. Under these conditions the band spectral contour becomes different from what it is at low pressures, and one can no longer use the low-pressure values for high-pressure predictions. This effect should be considerably more important at low temperatures, where the bands are narrow and the lines near the band centers are much stronger than those in the wings, than at high temperatures, where the bands are very broad and tend to run smoothly into one another and where central and wing line strengths are much less different. At very high pressure (depending upon the temperature considered), the results of the upper-limit calculation are less reliable. In a later section we discuss our estimate of where this line wing effect is significant.

We may sum up by saying that the total emissivity determined by extrapolation of thin-gas spectral emissivity measurements is exact (within the limits of errors in measurements) at small values of the pathlength, and represents an upper limit, subject to certain qualifications, approached at high pressures and/or temperatures for larger values of pathlength. A sufficient condition that the observed gas is optically thin is that the apparent integrated intensities of all vibration-rotation bands, determined from the observed data, be very nearly equal to the value obtained in the limit as $p_e l \rightarrow 0$. (This condition is somewhat less stringent than requiring $(kp_e l) \ll 1$ everywhere. A single group of strong lines may give rise to large values of $(kp_e l)$ at some wavenumbers; however, if the effects on the integrated band intensities are small, the effects of total emissivity will also be small).

One is normally interested in the emission from hot water vapor at the temperatures produced in combustion systems—flames, furnaces, engines, and rocket exhausts—which may range between 500° and 3000°K. At these temperatures most of the energy radiated by a blackbody falls at wavelengths longer than 0.9 microns, or at wavenumbers below 11 000 cm^{-1} . At low or moderate optical depths, a larger fraction of the emission from water vapor occurs

at the longer wavelengths than does emission from a blackbody at the same temperature; as the optical depth increases, the H_2O emission approaches that of a blackbody. We therefore conclude that we may replace the upper limit of integration in equation (2) by 11 000 cm^{-1} to a very good approximation, thereby avoiding having to consider the very high-order emission bands of water below 0.9 μ . The important bands of H_2O in this region are the pure rotational band, the fundamental rotation-vibration bands at 6.3 μ and 2.7 μ , and the vibration-rotation overtone-combination bands at 1.87 μ , 1.34 μ , and 1.1 μ .

TREATMENT OF EXPERIMENTAL DATA

Spectral emissivities of the vibration-rotation bands and of the high-frequency side of the pure rotation band have been measured [8-11] at a total pressure of 1 atm, temperatures between 530° and 2250°K, and at optical depths between 0.8 and 2.34 cm atm of H_2O . (By coincidence, the measurements happened to be made with a very nearly constant mass of H_2O per unit area in the optical path, i.e. $\rho l \approx 2.4 \times 10^{-4} \text{ g cm}^{-2} \pm 5$ per cent.) The integrated intensities of the vibration-rotation bands, at temperatures greater than 1500°K, determined from these data and corrected for the temperature dependence of overtone and combination bands [12], generally agree well with the data obtained by other investigators [13-15] using quite different techniques. At temperatures below 1500°K, the stronger bands show apparent integrated intensities which are less than the correct value, indicating that under these conditions insufficient broadening has occurred. The present data were measured in gases produced at the exit of a small rocket motor with a contoured nozzle designed to produce a uniform exhaust. Details of the experimental technique may be found in previous publications [8-11]. Typical results (synthesized from measurements of the various band systems) are shown in Fig. 2, where the quantity $-\ln(1 - \epsilon)$ is plotted versus wavenumber. The experimental error in measured

spectral emissivity varies somewhat over the spectrum, but is ± 10 per cent in most cases.

From the measured emissivity values, one may determine an apparent absorption coefficient, Z , by inverting equation (2):

$$Z(\nu, T) = \frac{1}{p_e l} \ln \frac{1}{1 - \epsilon} \quad (3)$$

At high temperatures, Z approaches \bar{k} , the "true" absorption coefficient frequency-averaged over

In the case of the vibration-rotation bands, the correction is made by use of the expression for the spectral emissivity of a gas represented by the statistical [3, 4] band model with collision-broadened lines. In this case

$$Z(\nu) = \bar{k} / \sqrt{1 + \bar{k} p_e l / 4a}, \quad (4)$$

where a is the ratio of the line half-width to the mean line spacing. Here both \bar{k} and a are functions of temperature, wavelength, and partial

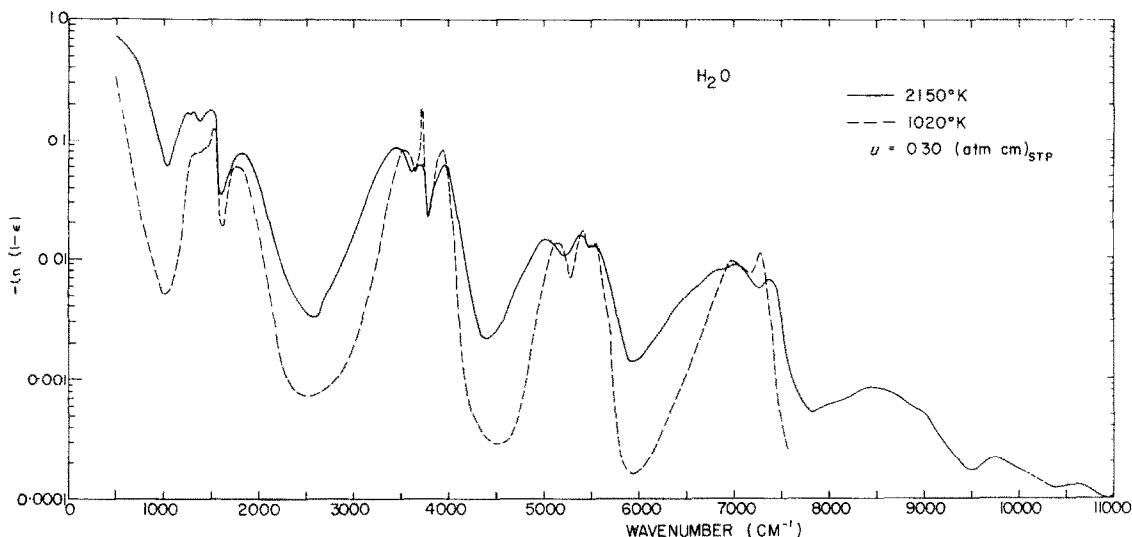


FIG. 2. Spectral emissivities of hot water vapor. Plot of $-\ln(1 - \epsilon)$ vs. wavenumber from the measurements of the authors.

a small interval. At lower temperatures, appreciable effects of spectral fine structure occur, so that $Z \neq \bar{k}$. The aim of the present investigation is two-fold: first, determination of exact total emissivities for our observed systems; second, determination of values of the total emissivity of water vapor which are exact at low path-lengths and which represent an absolute upper limit at moderate and long paths. We may therefore use the high-temperature values directly in equation (2) to determine emission from high-temperature water, but the low-temperature values require correction in order to be used in the second calculation.*

* It was not possible to make the optical depth small enough so that the gas was always thin without introducing inhomogeneities into the hot gas sample.

pressures of the various constituents of the gas. In principle, the determination of "true" values of \bar{k} and a from measured data requires measurements on samples of at least two different path-lengths at the same temperature, partial pressure, and wavelength. At present, however, such data are not available, and another approach is taken. Here the values of a are averaged over the band to provide an "effective" band value, \bar{a} . The values of \bar{k}_{app} at small wavenumber intervals and of \bar{a} for the band are then determined from equation (4), with the conditions that the integrated band intensity be equal to that determined from the high-temperature data, i.e.

$$\int_{\text{band}} \bar{k}_{app}(T, \nu) d\nu = \alpha(T). \quad (5)$$

Because of the use of a band-averaged \bar{a} , \bar{k}_{app} is

not truly \bar{k} . However, since \bar{k}_{app} was determined in part from an integral relation, equation (5), its use in another integral relation, equation (1), should not lead to large errors provided that N_v^0 , the blackbody function, does not vary too greatly over the band. This procedure has been applied to the 6.3- and 2.7- μ bands* of H_2O ; correction of the overtone and combination bands was unnecessary because we can assume that these bands are "thin". Values of $\bar{a}(T)$ below 1500°K for the various bands are close to those expected for H_2O from theoretical considerations [16]. At temperatures above 1500°K, values of \bar{a} cannot be determined from the data at hand, but they are not required for these cases for our present purpose, since no fine structure effects are apparent.

In the case of the pure rotation band, only the high-wavenumber side of the band has been measured. The values of \bar{k} for this band are specified by an analytical function which is determined from theoretical considerations using the just-overlapping line model. The calculation is complicated by the fact that the H_2O molecule is asymmetric, so that no simple expression for the rotational energy levels exists. The expression which we have employed has been developed in detail elsewhere [11], and we shall only discuss its qualitative features here. The crucial assumption is the replacement of the asymmetric top line strength by the weighted mean of line strengths calculation for equivalent symmetric and "most asymmetric" tops. The resulting integrated intensity of the rotational band is $1800 \text{ cm}^{-2} \text{ atm}^{-1}$ at 273°K, which may be compared with values of 200 and $300 \text{ cm}^{-2} \text{ atm}^{-1}$ for the very prominent 2.7- and 6.3- μ bands. Values of \bar{a} which lead to reasonable agreement between calculated and measured emissivities are found to be comparable in

magnitude to those found for the vibration-rotation bands. The analytical expression for \bar{k} has been used to extend the measured data to very low wavenumbers, and also to represent the pure rotation spectrum in calculating the upper-limit total emissivities. We estimate a maximum-possible error of ± 20 per cent for the calculated upper-limit emission in the rotational band caused by approximations in our analytic expression. This causes an error of ± 10 per cent in the upper-limit emissivity in the worst case, and much less in most situations.

We remarked previously that at extremely high pressures our upper-limit calculations are potentially subject to error because of the effects of great broadening of strong lines near the band center. These lines then contribute more strongly to emission in the band wings than do the wing lines themselves, and so the spectral contour of the band changes such that the true upper-limit total emissivity becomes larger than our calculated values. We have estimated the pressure at which this effect contributes, at the very most, 20 per cent to the emission in that valley between bands to which the total emissivity is most sensitive at various temperatures. The analysis is somewhat similar to that of Penner and Thomson [6]. The absorption coefficient in the wings at this pressure is assumed to be made up of wing line contributions and those of lines centered near the band center. The resulting expression for the limiting pressure (in atm) is

$$P = \pi^2 \bar{k}_w(T/300) / \sum_i [\alpha_i / (v_w - v_{c,i})^2], \quad (6)$$

where \bar{k}_w is the mean absorption coefficient at a wavenumber v_w at the bottom of a valley between bands, T is the temperature in °K, and α_i the integrated intensity of the i th band centered at the wavenumber $v_{c,i}$.

Equation (6) can be evaluated numerically by use of the absorption coefficients [17] determined from the spectral emissivity data given by Ferriso and Ludwig. We consider that the valley region which has the greatest effect upon

* Professor W. S. Benedict has pointed out (in a private communication) that the 6.3- μ band of water might not be expected to exhibit a constant value of the density-corrected integrated intensity because of very strong vibration-rotation interaction effects. However, no estimate of the magnitude of these effects has been made.

the total emissivity will be that lying nearest the spectral blackbody emission peak (that is, at temperatures between 1000° and 1500°K, the valley between the 6.3- and 2.7- μ bands, and at temperatures between 1500° and 2000°K, the valley between the 2.7- and 1.84- μ bands). We choose \bar{k}_w and v_w accordingly to obtain the values of the pressure at which our absorption coefficients are 20 per cent in error in these valley regions. The results are tabulated in Table 1. We have not directly evaluated the

Table 1. Values of pressure above which the calculated "upper limit" emissivities may not be true upper limits

Temperature	Pressure
1000° K	60 atm
1500° K	180 atm
2000° K	400 atm

effect of an error of this magnitude in \bar{k} upon the total emissivity, since the effect depends upon both temperature and optical depth. However, we can say that the effect will always be less than 20 per cent, and much less at optical depths low enough so that the wings contribute little to the total emission.

Our limiting pressure estimate assumes that H₂O is the principal broadening agent. Since H₂O is a more effective broadener of H₂O lines than other gases, systems dilute in H₂O will follow our upper-limit estimate to higher pressures better than will pure water. The reader should note that the pressures required to invalidate the upper-limit prediction are considerably higher at high temperature. This effect is primarily a consequence of the increase in \bar{k}_w caused by the overlapping of the band wings, which is apparent in all our experimental spectra above 1000°K.

RESULTS

Total emissivity at experimentally observed optical paths

Our spectral emissivity data have been integrated for the experimental conditions listed

in Table 2. The integration limits were from 450 cm⁻¹ to 11000 cm⁻¹, the region in which measurements were taken. The contribution of the rotational band beyond 450 cm⁻¹ has been included by using the analytical expression [11]

Table 2. List of experimental conditions and total emissivity determinations

T (° K)	p_e^l (cm atm)	u (cm atm) STP
550	0.66	0.33
1000	1.06	0.29
1400	1.44	0.28
1800	1.86	0.28
2250	2.40	0.29

together with a value of \bar{a} consistent with the experimental data in the spectral region from 450 cm⁻¹ to 1000 cm⁻¹. The results of this integration are shown in Fig. 3 as triangular points with ± 10 per cent error limits. In the same figure, the data from Hottel's tables are given as a solid curve up to 1900°K. Beyond this temperature, the dotted curve represents the

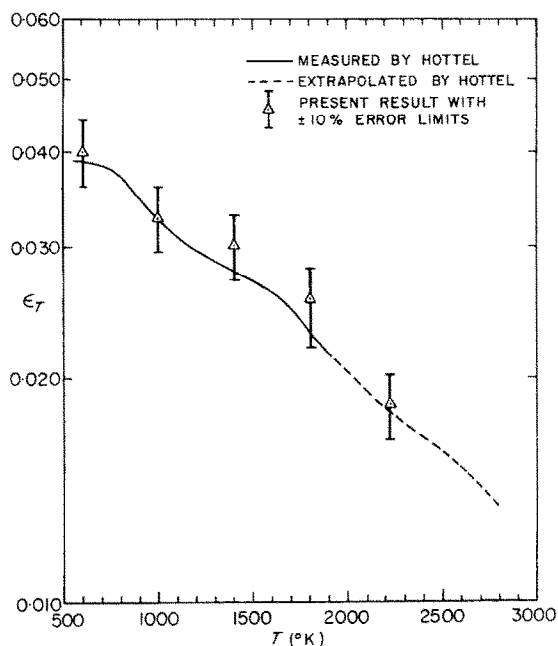


FIG. 3. Total emissivities by direct integration of spectral data. Comparison of the authors' results with Hottel's measurements of ϵ_T for H₂O.

extrapolation as given by Hottel. It is evident that good agreement exists between Hottel's and our data, even where Hottel's data were extrapolated. The fact that our standardized optical path u is not quite constant is reflected in the wavy form of the curve.

Extrapolation of the total emissivity to other optical paths

The experimentally determined data have also been used to determine an "exact" value of the thin-gas total emissivity per cm atm of H_2O .

expect the emissivity of a given thin sample of H_2O to be independent of gas composition and to depend only on temperature and the optical depth $p_e l$, where p_e is the partial pressure of H_2O . In Fig. 4 we show the thin-gas total emissivity per cm atm of H_2O as a function of temperature. This quantity is equivalent to

$$c_T/p_e l = \frac{\pi}{\sigma T^4} \int_0^{\infty} k(\nu, T) N_{\nu}^0(T) d\nu, \quad [kp_e l \ll 1]. \quad (7)$$

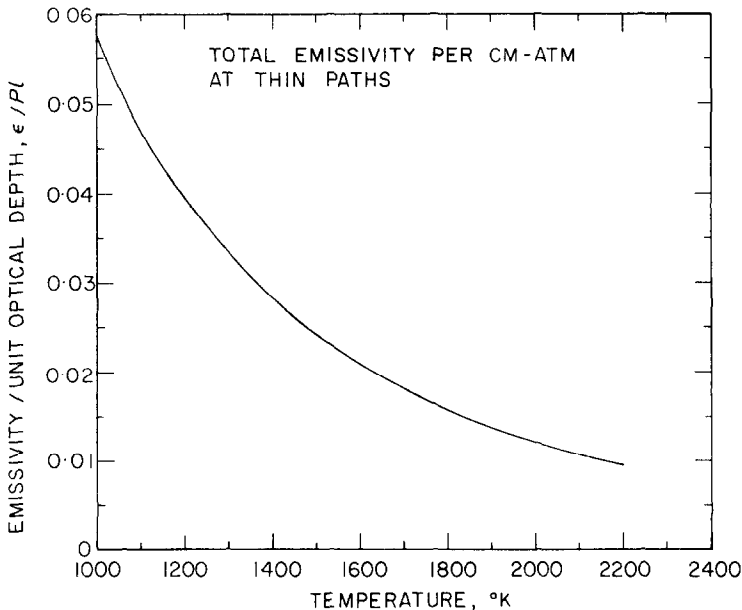


FIG. 4. Total emissivity of hot water vapor (per cm atm of optical depth) for very thin paths (≤ 0.2 cm atm) as a function of temperature.

The data given by Hottel are somewhat misleading at very thin pathlengths. Use of his chart for C_w would result in an emissivity for a this gas which depends on the relative proportions of H_2O and foreign-gas broadeners in the sample. Since collision broadening does not affect the emission from a thin gas,* we should

* Broadening of a spectral line in a dilute gas reduces the peak intensity and increases the line width, but does not affect the amount of energy radiated by the transition giving rise to the line.

A direct comparison with Hottel's data is not possible for the reasons cited.

Use of the absorption coefficients derived from the spectral emissivity data in equation (1) gives values of the total emissivity at greater optical depths which are, within the qualifications of the previous section, an upper limit to the total emissivity. We should expect these values to be approached as the total pressure of the samples is increased to values of the order of 1–10 atm. These data are presented in the

same manner employed in Hottel's chart in Fig. 5. These upper-limit values of the total emissivity are independent of composition.

Penner and Varanasi [7] have suggested that at pressures greater than about 1 atm of pure water vapor, emission from H_2O should be pressure-broadened. We would then expect our

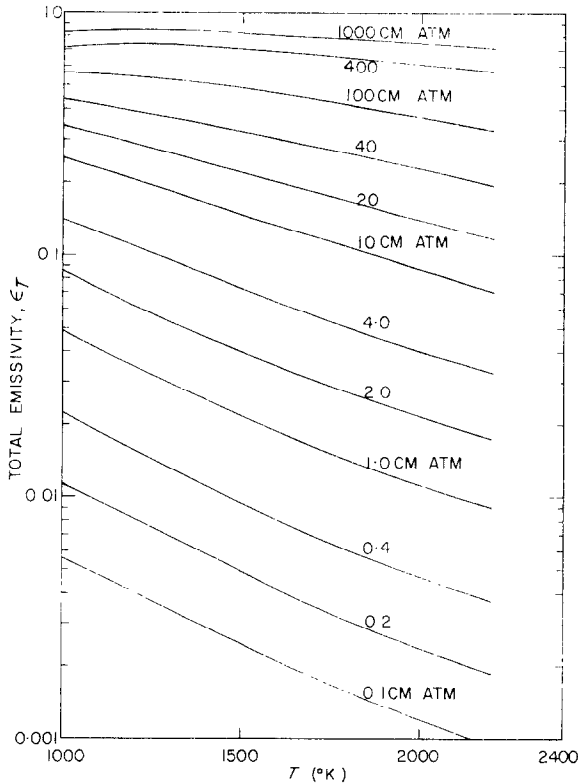


FIG. 5. Total emissivities of hot water vapor at high pressures. Upper limit to ϵ_T at low pressures.

upper-limit calculation to be in good agreement with the Hottel values at this condition. In Fig. 6 we show a comparison between our calculation and Hottel's data, where we have employed his correction C_w to adjust his data to 1 atm of pure water vapor. At low optical depths ($\frac{1}{4}$ ft-atm and below) our calculation is very close to and slightly above the Hottel data. At greater optical depths values from our calculation are somewhat more different from the observation, and always above it. A possible

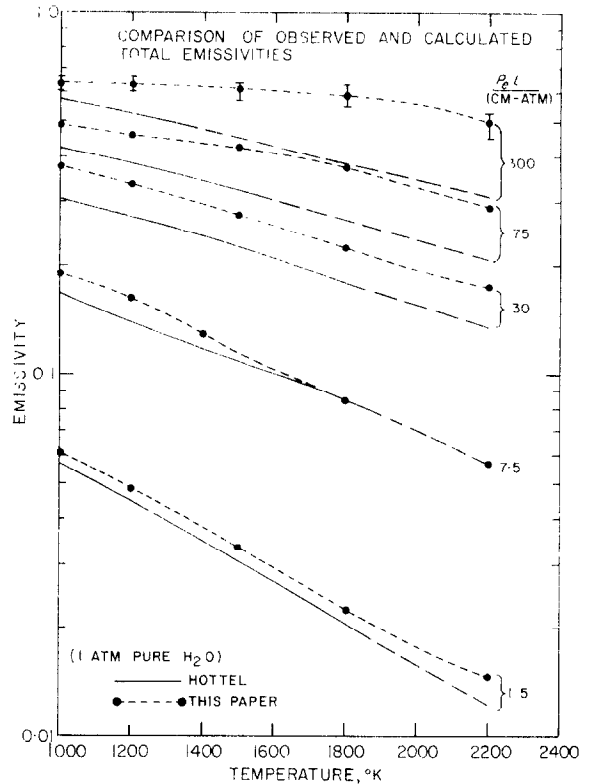


FIG. 6. Comparison of the upper-limit or high-pressure total emissivities of H_2O with Hottel's values at a pressure of 1 atm.

conclusion from this comparison is that pressures somewhat greater than 1 atm are required in order that the H_2O emissivity approaches its limit at high pressures.

That this difference is outside the range of error in our experimental data can easily be shown. A comparison between values of the integrated intensities of H_2O bands measured by us and by Goldstein [13, 14] indicates that the uncertainties in this quantity are of the order of 20 per cent. In the top curve we have indicated as error flags on our calculated points the effects of increasing or decreasing the integrated intensities of all bands by 20 per cent. The emissivity is affected by much less than 20 per cent, because a large part of the spectrum is saturated.

Another interesting comparison is that between our calculation and that of Penner and

Varanasi. These authors used a simple rigid-rotator expression for the absorption coefficient in a just-overlapping line calculation. The integrated intensities of the various bands were allowed to vary with temperature according to the harmonic oscillator approximation [12]. In Fig. 7 we show a comparison between the two

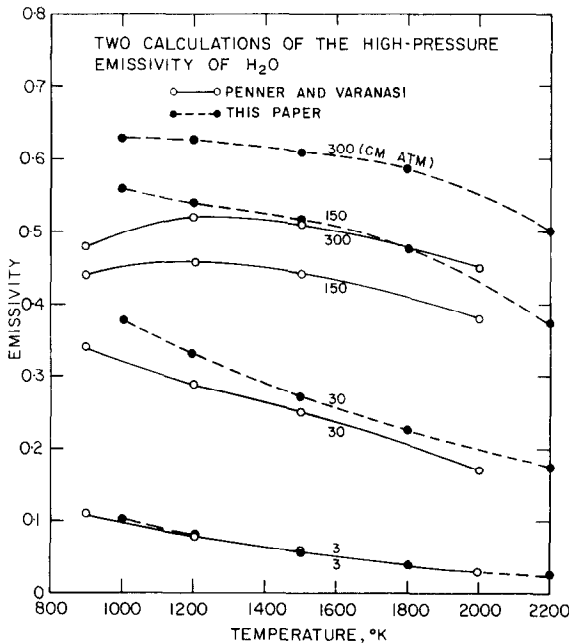


FIG. 7. Comparison of two upper limit calculations for the total emissivity of H_2O .

calculations. They are seen to be nearly equivalent at low optical depths (where both, according to Fig. 6, agree well with Hottel's data). At larger optical depths there are some noticeable differences. We tentatively attribute these to the differences in band shape given by the different approaches. At these optical depths the emissivity is mostly sensitive to the band wings, which are probably better represented in our experimental data. However, at temperatures above about $1200^\circ K$ the Penner-Varanasi calculation is above Hottel's data, as is ours, and therefore can be used for estimating the upper limit to ϵ_T or its high-pressure value when accuracy of 20-25 per cent is required. For more accurate work, we recommend our results.

SUMMARY AND CONCLUSIONS

We have shown how the total emissivity of water vapor can be determined from detailed spectral measurements of H_2O emission. The measurements were performed on H_2O samples which were either optically thin or somewhat optically thick (but not extremely thick). The observed spectral emissivities were corrected in order to obtain \bar{k} , the absorption coefficient frequency-averaged over a spectral interval of a few wavenumbers. The emissivities of hot water vapor were calculated first by direct integration of our observed data; these emissivities agree well with Hottel's data. We then determined the thin-gas emissivity per unit pathlength. Lastly, we used the values of \bar{k} to calculate the total emissivity at fairly large optical depths. This last calculation gives the true emissivity at high pressures and the upper limit to the emissivity at low pressures. A comparison with the data of Hottel indicates that the upper limit is not yet achieved at pressures near 1 atm when the optical depth is large. Comparison with the equivalent approximate calculation given by Penner and Varanasi shows qualitative agreement between the two calculations.

We recommend the use of the results of our final calculation when the following conditions pertain:

- (1) Pressures somewhat greater than 1 atm for pure H_2O or 5 atm for systems dilute in H_2O . (However, application to pressures greater than those listed in Table 1 may give values of ϵ_T which are somewhat low).
- (2) When a conservative estimate (in the sense of giving maximum heat transfer) is required for systems at atmospheric pressure or less in temperature and pathlength regimes where large extrapolations of Hottel's measured data are necessary.

Under other conditions one should use Hottel's data or the correlations of other investigators.

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Résumé—Des mesures de l'émissivité dans l'infrarouge de la vapeur d'eau à une température comprise entre 1000°K et 2250°K servent à déterminer l'émissivité totale de H₂O. L'émissivité totale est déterminée ici (1) d'une façon exacte pour les conditions expérimentales auxquelles les mesures ont été faites et (2) d'une façon approchée en obtenant une limite supérieure pour l'émissivité à des épaisseurs optiques différentes de celles des mesures. La première détermination fournit des résultats s'accordant tout à fait bien avec les valeurs de l'émissivité totale donnée par Hottel aux mêmes conditions. Les limites supérieures obtenues par la seconde détermination seront vraisemblablement voisines de l'émissivité réelle aux températures et aux pressions élevées. Quelques comparaisons rapides sont présentées ainsi que d'autres prévisions de l'émissivité totale de la vapeur d'eau sous ces conditions.

Zusammenfassung—Kürzlich durchgeführte Messungen der Infrarotspektralemission von heissem Wasserdampf bei Temperaturen zwischen 1000°K und 2250°K dienen zur Bestimmung der Gesamtemission von H₂O. In dieser Arbeit wurde die Gesamtstrahlung bestimmt: (1) exakt für die Versuchsbedingungen, bei welchen die Messungen durchgeführt wurden, und (2) in einer Näherung, welche die obere Grenze der Emission liefert bei optischen Tiefen, die von jener der Messungen abweichen. Die erste Bestimmung führt zu Ergebnissen, die ziemlich gut mit den Werten der Gesamtstrahlung übereinstimmen, die unter gleichen Bedingungen von Hottel angegeben wurden. Die oberen Grenzwerte der zweiten Bestimmung sollen die wahre Emission bei hohen Temperaturen und Drücken angenähert wiedergeben. Einige kurze Vergleiche mit anderen Bestimmungsmethoden der Gesamtstrahlung von Wasserdampf sind unter diesen Bedingungen gemacht.

Аннотация—Проведенные в последнее время измерения инфракрасной спектральной излучательной способности нагретого водяного пара при температурах от 1000°K до 2250°K использованы для определения полной излучательной способности H₂O. В настоящей работе полная излучательная способность определяется: (1) точно для условий эксперимента, при которых проведены измерения, и (2) в приближении, которое позволяет определить верхний предел излучательной способности для оптических глубин, отличный от полученного с помощью измерений.

В первом случае достигнуты результаты, хорошо согласующиеся с данными полной излучательной способности, полученными Хоттелем при тех же условиях. Предполагается, что значения для верхнего предела во втором случае близки к значениям истинной излучательной способности при высоких температурах и давлениях. Приводится краткое сравнение с другими расчетами полной излучательной способности пара при этих же условиях.