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Analytical Procedure for Evaluating the Emissivities of CO₂-H₂O Mixtures*

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In the radiative heat transfer of gas bodies it often becomes necessary to estimate the emissivities of mixtures, because the gas body would exist in the form of mixtures rather than of pure constituents in the practical engineering problems of interest.

The current study presents an evaluation procedure of the emissivities of CO₂-H₂O mixtures on the basis of the tentative physical models about the interactions of radiation embodied in the spectroscopic analyses of carbon dioxide and water vapour and also includes the results of the evaluation. The wavelength regions of important overlapping of vibration-rotation bands are substantially restricted to CO₂-2.7 μ band versus H₂O-2.7 μ band and CO₂-15 μ band versus H₂O-10 μ ~pure rotations.

In consequence the comparison of calculation results of the interaction term $\Delta\epsilon$ with the Hottel's data indicates a pertinent consistency.

It facilitates the estimation of $\Delta\epsilon$ under an arbitrary physical condition (say, temperature, optical length, mixture ratio, etc.) and these results are applicable to the various important problems in the radiative heat transfer.

1. Introduction

It is necessary to estimate rigorously the emissivities of gas mixtures in evaluating the radiative heat from the hot gases. Generally the gas body obeys the selection rule for the wavelength of the radiant ray and if the radiant rays that are emitted from one component of mixtures are opaque for the other components, the crucial interaction such as absorption or re-emission might occur and in consequence the total emissivity of gas mixture will become smaller than that of the total summation of the individual emissivity of the pure component. There is, however, no universal procedure for evaluating the emissivities of gas mixtures taking into consideration the overlapping mechanism of the spectral bands. As the overlapping situation depends on the kind of mixture and also on the wavelength range for the same gas mixture an appropriate treatment should be introduced for each problem. Besides it is well known that the total emissivities including the foreign infrared-inactive gases such as O₂ and N₂ are affected, even under the same optical length, by the molecular collisions which cause the inert gas broadening of the spectral line.

The present paper makes some spectroscopic discussions about the interaction mechanisms between CO₂ and H₂O and shows an analytical procedure for evaluating the emissivities of CO₂-H₂O mixtures. For the carbon dioxide and water vapour the interaction phenomena are observed in the wavelength regions around about 2.7 μ and longer than 10 μ respectively. The detailed mechanism of the interaction seems to be still veiled. It has been known for many years that the total emissivity has to be corrected from the simply added emissivity of the pure constituent which is called here the interaction term, $\Delta\epsilon$, and that the numerical values of $\Delta\epsilon$ against mixture ratio are calculated by Hottel et al.⁽¹⁾ at various temperatures and optical lengths with reference to Eckert's study⁽²⁾. While these results have frequently been applied to many radiative heat transfer problems in combustion furnaces and are convenient for the practical purposes, it is nevertheless difficult to calculate the emissivity of gas mixture at an arbitrary physical condition (temperature, mixture ratio and optical length) and also to separate the interaction term into the two aforementioned wavelength regions so as to account for the radiative heat from a monochromatic viewpoint.

Accordingly the author proposes simplified models on the overlapping situations between the spectra

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bands without eliminating the essential features and shows the evaluation results on the basis of the band emissivities data⁽³⁾ which were formerly obtained by the authors.

2. Nomenclature

- A_1 : constant in Eq. (11)
 A_2 : constant in Eq. (20)
 c : light velocity
 F_i : bandwidth function of i -th interaction wavelength range, Eq. (9)
 h : Planck constant
 k : Boltzmann constant
 m : reciprocal power index
 n : reciprocal power index
 p : pressure
 T : absolute temperature
 T_0 : standard temperature
 X : optical length (cm·atm)
 X_0 : standard optical length (cm·atm)
 α_i : i -th integrated absorption coefficient
 $\epsilon_{b,i}$: i -th band emissivity
 ϵ_{lim} : limiting emissivity
 ϵ_λ : spectral emissivity
 $\Delta\epsilon$: interaction term
 λ : wavelength (μ)
 λ_c : wavelength at band centre
 λ_0 : wavelength defined in Eq. (11)
 $(\Delta\lambda)_i$: i -th wavelength range of interaction
 κ_λ : spectral absorption coefficient
 ν_1, ν_2, ν_3 : fundamental frequency of tri-atomic molecule ($\text{CO}_2, \text{H}_2\text{O}$)
 σ : Stefan Boltzmann constant
 ω : wavenumber (cm^{-1})
 ω_0 : wavenumber at band centre

3. Band emissivities of carbon dioxide and water vapour

As already stated the author enunciated an analytical procedure for determining the band emissivities of carbon dioxide and water vapour⁽³⁾. In this article the analytical procedure is briefly reviewed and some evaluation results on the interaction of $\text{CO}_2\text{-H}_2\text{O}$ bands are illustrated.

Some spectroscopic discussions were held on the locations, bandwidths and configurations of the spectral bands and thereafter the limiting emissivities with the infinite optical length were obtained. The tentative absorption coefficients for vibration-rotation band are, then, determined in accordance with total emissivities data by Hottel et al. Consequently the limiting emissivity ϵ_{lim} , band emissivity $\epsilon_{b,i}$ and total emissivity ϵ_{total} are expressed in the following equations.

$$\epsilon_{lim} = \frac{2\pi hc^2 \omega_0^3}{\exp(hc\omega_0/kT) - 1} \Delta\omega / \sigma T^4 \dots\dots\dots (1)$$

$$\epsilon_{b,i} = \frac{2\pi hc^2 \omega_0^3}{\exp(hc\omega_0/kT) - 1} \Delta\omega \times \left\{ 1 - \exp\left(-\frac{\alpha_i}{\Delta\omega} X\right) \right\} / \sigma T^4 \dots\dots\dots (2)$$

$$\epsilon_{total} = \sum_i \epsilon_{b,i} \dots\dots\dots (3)$$

Those data concerning the band emissivities, however, neither include the elaborate knowledges of the individual bandwidth nor the detailed information on the spectral absorption (emission) coefficients. Especially as the water vapour is an asymmetric top molecule the internal motions (vibrations and rotations) are complicated and the spectral line spacing is substantially greater than the linewidth. Thus, the spectroscopic treatments about the water vapour will eventually be formidable. But the final results obtained utilizing these emissivities are satisfactory, because the total emissivities calculated on the basis of the absorption coefficients which are determined at comparatively low temperature, show a fairly good coincidence with those of Hottel et al. over the physical conditions of interest.

The limiting emissivities of carbon dioxide and water vapour are reproduced in Figs. 1 and 2 respectively. An examination of these figures makes it clear that the interaction between $\text{CO}_2\text{-}15\mu$ band and $\text{H}_2\text{O-}10\mu \sim$ pure rotations has a significance at comparatively low temperature and the other bands.

Fig. 1 Limiting emissivities of carbon dioxide

Fig. 2 Limiting emissivities of water vapour

including the 2.7μ bands of CO_2 and H_2O do not participate in the interaction. Similarly it is also understood that as the temperature of the mixture is elevated the effect of the interaction in the longer wavelength range ($10\mu\sim$) gradually diminishes and simultaneously the interaction around 2.7μ becomes important. Figures 3 and 4 refer to the band emissivities of carbon dioxide and water vapour against the optical length that relate to the interactions (15μ band and 2.7μ band for CO_2 , $10\mu\sim$ rotations and 2.7μ band for H_2O).

In the following the quantitative treatment for spectroscopic mechanism of interaction will be developed and on this basis two different physical models for the calculation procedure will be introduced.

4. Interaction of radiation between carbon dioxide and water vapour

4.1 Interaction of mixture gas radiation

At first as a general problem the interaction of radiation of a two-component mixture will be considered, where one identifies the two constituents as A and B respectively. From a monochromatic view-

point at which the Lambert-Beer law should be valid, the following general expression is obtained:

$$\epsilon_i(\text{mixture}) = \epsilon_i(A) + \epsilon_i(B) - \Delta\epsilon_i \quad \dots(4)$$

For the spectral bands which concern the interaction the band emissivities of gas mixture are represented, putting the i -th wavelength range of interaction as $(\Delta\lambda)_i$, as follows:

$$\epsilon_{b,i}(\text{mixture}) = \epsilon_{b,i}(A) + \epsilon_{b,i}(B) - \Delta\epsilon_i \quad \dots(5)$$

where $\epsilon_{b,i}(A)$, $\epsilon_{b,i}(B)$ and $\Delta\epsilon_i$ are, respectively, expressed as follows:

$$\epsilon_{b,i}(A) = \int_{(\Delta\lambda)_i} \frac{2\pi hc^2 \omega_{0,i}^3}{\exp(hc\omega_{0,i}/kT) - 1} \epsilon_i(A) d\lambda / \sigma T^4 \quad \dots(6.a)$$

$$\epsilon_{b,i}(B) = \int_{(\Delta\lambda)_i} \frac{2\pi hc^2 \omega_{0,i}^3}{\exp(hc\omega_{0,i}/kT) - 1} \epsilon_i(B) d\lambda / \sigma T^4 \quad \dots(6.b)$$

$$\Delta\epsilon_i = \int_{(\Delta\lambda)_i} \frac{2\pi hc^2 \omega_{0,i}^3}{\exp(hc\omega_{0,i}/kT) - 1} \epsilon_i(A) \epsilon_i(B) d\lambda / \sigma T^4 \quad \dots(6.c)$$

It is apparent from Eq. (5) that if the interaction of the spectral bands is not observed the band emissivity is simply obtained by adding the band emissivities of the pure constituents, eliminating the third term $\Delta\epsilon_i$ of right hand side from Eq. (5).

The total emissivity of gas mixture ϵ_{total} (mixture) becomes eventually from Eq. (5) as follow:

$$\epsilon_{\text{total}}(\text{mixture}) = \sum_i \epsilon_{b,i}(\text{mixture}) = \epsilon_{\text{total}}(A) + \epsilon_{\text{total}}(B) - \Delta\epsilon \quad \dots(7)$$

where

Fig. 3 Band emissivities of carbon dioxide

Fig. 4 Band emissivities of water vapour

$$\Delta\epsilon = \sum_i \Delta\epsilon_i = \sum_i \int_{(\Delta\lambda)_i} \frac{2\pi hc^2 \omega_{0,i}^3}{\exp(hc\omega_{0,i}/kT) - 1} \times \epsilon_i(A) \epsilon_i(B) d\lambda / \sigma T^4 \dots\dots\dots (8)$$

The integration range $(\Delta\lambda)_i$ in Eq. (8) is generally a complex function of pressure, temperature, optical length, mixture ratio, etc. Thus,

$$(\Delta\lambda)_i = F_i(p, T, X, \dots) \dots\dots\dots (9)$$

Consequently it is necessary to reveal the detailed configurations of the spectral bands that are taking part in the interaction.

For the interaction problem between carbon dioxide and water vapour the overlappings of strong spectral bands are observed, as already stated, in the two wavelength regions and the overlapping situations are quite different from each other. In order to preform the integration of Eq. (8) suitable models must be constructed relating the wavelength range of interaction $(\Delta\lambda)_i$ to the temperature, optical length and mixture ratio and also reducing the spectral emissivities, $\epsilon_i(A)$ and $\epsilon_i(B)$, to simple mathematical formulations. Before introducing the heuristic physical models embodied in Eqs. (8) and (9) the overlapping situations of CO₂ and H₂O bands in the two wavelength regions deserve closer look. The interaction mechanism will be examined in the following two sections. The suffix i equals 1 for the interaction of the wavelength range longer than 10 μ and i equals 2 for that of around 2.7 μ .

4.2 Interaction between CO₂-15 μ band and H₂O-10 μ ~ pure rotations

The CO₂-15 μ band is due to the transition of one of the three fundamental vibrational energy levels and its associated rotational energy levels, located at the wavelength around about 15 μ . One might express approximately the bandwidth of CO₂-15 μ band, $(\Delta\lambda)_{\text{CO}_2-15\mu}$, against the temperature and the optical length in the form:⁽⁹⁾

$$(\Delta\lambda)_{\text{CO}_2-15\mu} / (\Delta\lambda)_0 = (T/T_0)^{1/2} (X/X_0)^{1/2} \dots\dots\dots (10)$$

where the suffix 0 denotes the standard value.

For the water vapour the pure rotational transitions (without the vibrational transition) are observed in the comparatively long wavelength range; however, it is convenient to regard the cluster of these rotational lines as forming a band, and effective bandwidth is considered so as to ignore the fine structure although the fine rotational lines are not smeared out at moderate pressure because of the large line spacings.

Figure 5 shows the typical results on the spectra of CO₂-15 μ band and H₂O-10 μ ~ rotations. In this figure λ_1 and λ_2 ($\lambda_1 < \lambda_2$) denote the wavelengths where emission spectrum of CO₂-15 μ band becomes substantially zero, and further λ_0 means the similar wavelength for H₂O-10 μ ~ rotations. Reference to Fig. 5 shows that water vapour with small optical length

is transparent in the wavelength range from 13 μ to 17 μ where CO₂-15 μ band is located and that as the optical length of H₂O increases the water vapour becomes opaque gradually for CO₂-15 μ band. In other words the wavelength range of H₂O-10 μ ~ rotations expands toward the shorter wavelength as the optical length of water vapour increases. Hence it might be possible to simplify the overlapping mechanism by introducing an appropriate physical model which leads to the mathematical formulation on the interaction term $\Delta\epsilon_i = \Delta\epsilon_1$ ($i=1$). A most direct and empirical approach is to assume that a band shape for the H₂O-10 μ ~ rotations can be treated as a straight line neglecting the rotational fine structure and that a wavelength λ_0 , where spectral emissivity is substantially zero, is a simple function of temperature and optical length.

Actually the spectral emissivity of H₂O-10 μ ~ rotations $\epsilon_2(\text{H}_2\text{O}-10\mu\sim)$ is assumed to be

$$\epsilon_2(\text{H}_2\text{O}-10\mu\sim) = A_1(\lambda - \lambda_0) \dots\dots\dots (11)$$

where A_1 means the slope of spectral emissivity against wavelength and considered to be constant from Fig. 5. The numerical value of A_1 is approximately 0.115(μ^{-1}). The spectral emissivity is regarded to be unity for the wavelength range where $\epsilon_2(\text{H}_2\text{O}-10\mu\sim)$ in Eq. (11) yields a value above unity.

Consequently the wavelength range of interaction between CO₂-15 μ band and H₂O-10 μ ~ rotations can be calculated by combining Eq. (10) with Eq. (11). Similarly to Eq. (10) the bandwidth of H₂O-10 μ ~rotations $(\Delta\lambda)$ is also assumed, considering the cluster of rotational spectra to from a band,

$$(\Delta\lambda) / (\Delta\lambda)_0 = (T/T_0)^{1/m} (X/X_0)^{1/n} \dots\dots\dots (12)$$

and then the wavelength λ_0 is expressed as a function of temperature and optical length, i.e.

$$\lambda_0 = \lambda_c - \frac{(\lambda)_0}{2(T_0)^{1/m}(X_0)^{1/n}} (T)^{1/m} (X)^{1/n} \dots\dots\dots (13)$$

In this equation λ_c is a wavelength at band centre provisionally used for convenience and the suffix 0 denotes the value at standard condition. The numerical values of m , n and λ_c are determined to be 2, 3 and 25 (μ) by examining the spectra in reference

Fig. 5 Interaction between CO₂-15 μ band and H₂O-10 μ ~ rotations

(4). Further an assumption is introduced for

$$\begin{aligned}\Delta\epsilon_i(\text{CO}_2\text{-}15\mu\sim\text{H}_2\text{O}\text{-}10\mu\sim) &= \Delta\epsilon_i; \\ \Delta\epsilon_i &= \int_{(\Delta\lambda)_1} \epsilon_i(\text{CO}_2) \epsilon_i(\text{H}_2\text{O}) d\lambda \\ &\cong \epsilon_{b,i}(\text{CO}_2\text{-}15\mu) \int_{(\Delta\lambda)_1} \epsilon_i(\text{H}_2\text{O}\text{-}10\mu\sim) d\lambda \dots (14)\end{aligned}$$

This assumption is based on the concept that as the band centre of $\text{CO}_2\text{-}15\mu$ band is scarcely changed by the variation of temperature and optical length, the overlapping situation is mostly dependent on the spectral behavior of $\text{H}_2\text{O}\text{-}10\mu\sim$ rotations and that an exact treatment taking account of the complex spectral emissivities is tremendously difficult so that the band emissivity data are sufficient for the present purpose of evaluating the interaction term.

It should be borne in mind that the simple product of the band emissivities of $\text{CO}_2\text{-}15\mu$ band and $\text{H}_2\text{O}\text{-}10\mu\sim$ pure rotations could not yield any correct interaction term (in fact, it is easily confirmed to be inappropriate) and that a suitable analytical model based on the spectroscopic overlapping mechanism could facilitate the calculation of $\Delta\epsilon_i$.

It is summarized for the interaction model in the wavelength range longer than 10μ as follows. While the $\text{CO}_2\text{-}15\mu$ band locates around the wavelength of 15μ , the $\text{H}_2\text{O}\text{-}10\mu\sim$ pure rotations appear in far infrared region in case of the small optical length of water vapour and then no interaction is found between $\text{CO}_2\text{-}15\mu$ band and $\text{H}_2\text{O}\text{-}10\mu\sim$ rotations. As both the temperature and optical length of H_2O increase, the rotational spectra of H_2O extend toward the shorter wavelength as is indicated in Eq. (13), and the rotational spectra of H_2O come to interact with the $\text{CO}_2\text{-}15\mu$ band. Accordingly putting the bandwidth of $\text{CO}_2\text{-}15\mu$ band as $(\lambda_{2,\text{CO}_2\text{-}15\mu} - \lambda_{1,\text{CO}_2\text{-}15\mu})$ the wavelength range of interaction $(\Delta\lambda)_1$ which appears in Eq. (14) may be written in the form

$$(\Delta\lambda)_1 = \begin{cases} 0 & : (\lambda_{2,\text{CO}_2\text{-}15\mu} \leq \lambda_0) \dots\dots\dots (15\cdot a) \\ (\lambda_{2,\text{CO}_2\text{-}15\mu} - \lambda_0) : & \\ (\lambda_{1,\text{CO}_2\text{-}15\mu} \leq \lambda_0 \leq \lambda_{2,\text{CO}_2\text{-}15\mu}) & (15\cdot b) \\ (\lambda_{2,\text{CO}_2\text{-}15\mu} - \lambda_{1,\text{CO}_2\text{-}15\mu}) : & \\ (\lambda_0 \leq \lambda_{1,\text{CO}_2\text{-}15\mu}) & \dots\dots\dots (15\cdot c) \end{cases}$$

Equation (14) together with Eqs. (13) and (15.a, b, c) becomes

$$\begin{aligned}\Delta\epsilon_i &= \begin{cases} 0 & \dots\dots\dots (16\cdot a) \\ \epsilon_b(\text{CO}_2\text{-}15\mu) \frac{A_1}{2} \left\{ \lambda_2 - \lambda_c + \frac{(\Delta\lambda)_0}{2} \right. \\ \quad \times \left(\frac{T}{T_0} \right)^{1/m} \left(\frac{X}{X_0} \right)^{1/n} \Big\}^2 & \dots\dots\dots (16\cdot b) \\ \epsilon_b(\text{CO}_2\text{-}15\mu) A_1 (\lambda_{2,\text{CO}_2\text{-}15\mu} - \lambda_{1,\text{CO}_2\text{-}15\mu}) \\ \quad \times \left\{ \lambda_{c,\text{CO}_2\text{-}15\mu} - \lambda_c + \frac{(\Delta\lambda)_0}{2} \left(\frac{T}{T_0} \right)^{1/m} \left(\frac{X}{X_0} \right)^{1/n} \right\} & \dots\dots\dots (16\cdot c) \end{cases}\end{aligned}$$

The band emissivities for this wavelength range being important at comparatively low temperature, the interaction term $\Delta\epsilon_i$ is evidently predominant at low temperature. The interaction term at arbitrary temperature can be evaluated by making use of Figs. 1 and 2.

4.3 Interaction between $\text{CO}_2\text{-}2.7\mu$ band and $\text{H}_2\text{O}\text{-}2.7\mu$ band

Putting the three fundamental frequencies of CO_2 vibration as ν_1 , ν_2 and ν_3 , the $\text{CO}_2\text{-}2.7\mu$ band consists of the combination bands $(2\nu_2 + \nu_3)$ and $(\nu_1 + \nu_3)$ and this band is well known to be favorable for the Beer's law, because its spectrum is observed to be continuous even with a high resolution spectrometer, due to an overlapping of spectral lines. The $\text{H}_2\text{O}\text{-}2.7\mu$ band consists of the two fundamentals ν_1 and ν_3 . This band does not look favorable for the Beer's law because of the greater line spacing than the line width at moderate pressure. Thus the complicated configuration of spectrum of $\text{H}_2\text{O}\text{-}2.7\mu$ band becomes cumbersome for a rigorous treatment of the interaction. The results⁽⁵⁾ of spectroscopic analyses for CO_2 and H_2O gases around about 2.7μ are reproduced in Fig. 6. These spectra were measured with a prism spectrometer, with the gases maintained at 1273°K in a heated quartz gas cell. For a gas at thermal equilibrium, spectral emissivity and spectral absorptivity are equal at every wavelength according to the Kirchhoff's law of radiation and therefore the spectral emissivities are illustrated instead of absorptivities in Fig. 6. Reference to the figure shows that the spectrum of $\text{H}_2\text{O}\text{-}2.7\mu$ band is in a wavelength range from 2.4μ to 3.2μ and the spectrum of $\text{CO}_2\text{-}2.7\mu$ band is from 2.65μ to 2.95μ . Though this situation is influenced by the variation of temperature and optical length it is generally concluded that the bandwidth of water vapour is always greater than that of carbon dioxide.

On this basis the author proposes a simplified interaction model for $\text{CO}_2\text{-}2.7\mu$ and $\text{H}_2\text{O}\text{-}2.7\mu$ bands which shown schematically in Fig. 7. The effective bandwidth is considered for water vapour and a constant spectral emissivity is assumed so as to elimi-

Fig. 6 Absorption spectra of CO_2 and H_2O at 2.7μ region⁽⁵⁾

nate the complicated rotational fine structure again. In this case, the entire band of CO₂-2.7 μ interacts with the H₂O-2.7 μ band. The band emissivities of CO₂-2.7 μ and H₂O-2.7 μ , i.e. $\epsilon_b(\text{CO}_2\text{-}2.7\mu)$ and $\epsilon_b(\text{H}_2\text{O-}2.7\mu)$ are rewritten in the form:

$$\epsilon_b(\text{CO}_2\text{-}2.7\mu) = \int_{\lambda_{1,\text{CO}_2}}^{\lambda_{2,\text{CO}_2}} \frac{2\pi hc^2 \omega_0^3}{\exp(hc\omega_0/kT) - 1} \times \{1 - \exp(-\kappa_{\lambda,\text{CO}_2} X_{\text{CO}_2}/RT)\} d\lambda / \sigma T^4 \dots (17)$$

$$\begin{aligned} \epsilon_b(\text{H}_2\text{O-}2.7\mu) &= \int_{\lambda_{1,\text{H}_2\text{O}}}^{\lambda_{2,\text{H}_2\text{O}}} \frac{2\pi hc^2 \omega_0^3}{\exp(hc\omega_0/kT) - 1} \times \{1 - \exp(-\kappa_{\lambda,\text{H}_2\text{O}} X_{\text{H}_2\text{O}}/RT)\} d\lambda / \sigma T^4 \\ &= \int_{\lambda_{1,\text{H}_2\text{O}}}^{\lambda_{1,\text{CO}_2}} \frac{2\pi hc^2 \omega_0^3}{\exp(hc\omega_0/kT) - 1} \times \{1 - \exp(-\kappa_{\lambda,\text{H}_2\text{O}} X_{\text{H}_2\text{O}}/RT)\} d\lambda / \sigma T^4 \\ &\quad + \int_{\lambda_{1,\text{CO}_2}}^{\lambda_{2,\text{H}_2\text{O}}} \frac{2\pi hc^2 \omega_0^3}{\exp(hc\omega_0/kT) - 1} \times \{1 - \exp(-\kappa_{\lambda,\text{H}_2\text{O}} X_{\text{H}_2\text{O}}/RT)\} d\lambda / \sigma T^4 \\ &\quad + \int_{\lambda_{1,\text{CO}_2}}^{\lambda_{2,\text{CO}_2}} \frac{2\pi hc^2 \omega_0^3}{\exp(hc\omega_0/kT) - 1} \times \{1 - \exp(-\kappa_{\lambda,\text{H}_2\text{O}} X_{\text{H}_2\text{O}}/RT)\} d\lambda / \sigma T^4 \dots (18) \end{aligned}$$

The interaction term $\Delta\epsilon_i(\text{CO}_2\text{-}2.7\mu \sim \text{H}_2\text{O-}2.7\mu) = \Delta\epsilon_2(i=2)$ can be calculated from Eq. (17) and the third term of the right hand side of Eq. (18). The wavelength range which concerns the interaction and the interaction term $\Delta\epsilon_2$ are respectively

$$(\Delta\lambda)_2 = \lambda_{2,\text{CO}_2} - \lambda_{1,\text{CO}_2}$$

$$\Delta\epsilon_2 = \int_{\lambda_{1,\text{CO}_2}}^{\lambda_{2,\text{CO}_2}} \epsilon_{\lambda}(\text{CO}_2) \epsilon_{\lambda}(\text{H}_2\text{O}) d\lambda \dots (19)$$

According to the model which is adopted here, the spectral emissivity of water vapour $\epsilon_{\lambda}(\text{H}_2\text{O})$ being constant for this wavelength range, the following approximation might be employed for Eq. (19):

$$\Delta\epsilon_2 = A_2 \epsilon_b(\text{CO}_2\text{-}2.7\mu) \epsilon_b(\text{H}_2\text{O-}2.7\mu) \dots (20)$$

where the constant A_2 means the ratio of the H₂O-2.7 μ band which interacts with CO₂-2.7 μ band to the whole band of H₂O-2.7 μ .

The interaction term for this wavelength range is of importance at high temperature and the magnitude of $\Delta\epsilon_2$ follows the variation of limiting emissivities against temperature (Figs. 1 and 2) in a similar manner to $\Delta\epsilon_1$.

5. Evaluation results and discussion

As already stated frequently the procedure for getting the emissivities of gas mixtures is to derive

the interaction terms in two wavelength regions independently and to obtain the total interaction term which is an addition of individual interaction terms. The other overlappings between weak bands of both carbon dioxide and water vapour are found; however, their contribution to the total interaction term is not significant except for the case of large optical length at high temperature, because these weak bands usually disappear at the ordinary physical conditions. Figure 8 is concerned with the first interaction term $\Delta\epsilon_1$ evaluated against mixture ratio. Some particular things of interest found in Fig. 8 are that the peak of $\Delta\epsilon_1$ deviates to the H₂O-rich mixture ratio [approximately $X_{\text{H}_2\text{O}}/(X_{\text{CO}_2} + X_{\text{H}_2\text{O}}) = 0.8$] and that there are certain ranges (lean mixture of H₂O with small optical length) where $\Delta\epsilon_1$ vanishes. These characteristic features qualitatively well corresponding to the Hottel's correlation, the analytical model introduced here might be regarded acceptable.

Meanwhile, the second interaction term, $\Delta\epsilon_2$, versus mixture ratio is illustrated in Fig. 9. It is quite reasonable from the inference of the proposed model that the configuration profile of $\Delta\epsilon_2$ is symmetric about mixture ratio.

For the purpose of examining the validity of the present analysis the calculated values of $\Delta\epsilon$ will be compared with empirical correlations by Hottel et al. and further with the results by Penner and Varanasi⁽⁶⁾ who recently analysed the effect of overlapping of the spectral lines on the total emissivity of H₂O-CO₂ mixtures at comparatively high temperature ($T \gtrsim 800^\circ\text{K}$) where they neglected the interaction term between CO₂-15 μ band and H₂O-10 $\mu \sim$ rotations. As far as the interaction at the wavelength around 2.7 μ is concerned, the model presented here is based on the assumption that the spectral absorption coefficient is constant within the described bandwidth ignoring the rotational fine structure, whereas the analytical model by Penner et al. is based on the assumption that the product of spectral coefficient κ_{λ} by optical length X being large one of the exponential quantities [i.e. $1 - \exp(-\kappa_{\lambda,\text{CO}_2} X_{\text{CO}_2}/RT)$ in Eq. (17) and $1 - \exp(-\kappa_{\lambda,\text{H}_2\text{O}} X_{\text{H}_2\text{O}}/RT)$ in Eq. (18)] is essentially constant in the spectral regions of vibration-rotation bands for which the

Fig. 7 Interaction model between CO₂-2.7 μ band and H₂O-2.7 μ band

second factor is substantially different from zero. Nevertheless they extrapolated the evaluation results to lower optical length.

Figure 10 shows comparisons of the values calculated from Eqs. (16) and (20) with both the empirical correlations by Hottel et al.⁽⁷⁾ and the calculated values by Penner et al. The results by Penner et al. are not included in Fig. 10 (a), as there is a limit of applicability to lower temperatures ($T \leq 800^\circ\text{K}$) because of the interaction in the $10\mu\sim$ region being neglected.

In the radiative heat transfer problems, however, the data on absorptivities at comparatively low temperature are important as well as those on high temperature emissivities. Reference to Fig. 10 shows that analytical results by Penner et al. rather than those evaluated in the present text correspond to empirical data by Hottel et al. at high temperature. This difference seems to be caused by the difference in band emissivity data because calculation procedures depend on essentially similar physical models. In fact, the results calculated by Penner et al. based on other band emissivities of Nelson are considered unacceptable. Further it is questionable that though Penner and Varanasi pointed out the discrepancy at comparatively low temperature owing to the uncertainty of the estimation of $\text{CO}_2\text{-}15\mu$ band versus $\text{H}_2\text{O-}10\mu\sim$ rotations, the values of $\Delta\epsilon$ calculated in reference (6) (where $\Delta\epsilon_1$ were neglected) are comparable to the empirical correlations. According to Figs. 8 and 9 $\Delta\epsilon_1$ and $\Delta\epsilon_2$ are approximately of the same magnitude.

Finally these results of $\Delta\epsilon$ do not necessarily show a good correspondence to Hottel's correlations for a wide range of parameters, but the results are generally acceptable. The author has the opinion that the major reason for the discrepancy is not the uncertainty of the absorption coefficient data but the veiled situation of the interaction mechanism be-

tween participating bands.

6. Conclusion

In the present study the band emissivities technique is applied to evaluating the engineering emissivities of gas mixtures by introducing simple and suitable interaction models which are based on the physical backgrounds. For the case of $\text{CO}_2\text{-H}_2\text{O}$ mixture two wavelength regions are considered separately and the total interaction term $\Delta\epsilon$ is estimated and examined comparing with the empirical data of Hottel et al. and the analytical results of Penner et al.

The resulting values and configuration profile of $\Delta\epsilon$ versus mixture ratio qualitatively resemble the Hottel's ones, particularly at low temperature so that the interaction model for $\text{CO}_2\text{-}15\mu$ band and $\text{H}_2\text{O-}10\mu$ rotations is suitable.

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