Thermal Diffusion in H_2 – CO_2 at High Pressures as Studied by Palladium Occlusion Method

T. K. S. NARAYANAN* AND G. DICKEL

Physikalisch-Chemisches Institut der Universität München

(Z. Naturforsch. **28a**, 290—292 [1973]; received 12. August 1972)

The thermal diffusion factor α of hydrogen-carbondioxide mixtures has been determined in two different ways by measuring the mole fractions as well as the partial pressures using a two bulb apparatus. The difference between the values of α has also been calculated thermodynamically and found to agree with the difference of the above values within experimental error.

1. Introduction and Problem

Besides the familiar definition of the thermal diffusion factor α given by the formula

$$\Delta\gamma_i = \gamma_i\,(1-\gamma_i)\ \alpha_\gamma\,\Delta T/T \qquad (i = 1,2) \qquad (1)$$

a definition as given by

$$\Delta p_i = p_i\,(1 - p_i\,/\,p)\ \alpha_{\mathrm{P}}\,\Delta T/T \qquad (i = 1,2) \qquad (2)$$

is also possible [1, 2]. γ_i is the mole fraction, p_i the partial pressure. ΔT indicates a local temperature difference in the stationary state. The difference between α_{P} and α_γ for real gases was obtained by Dikkel and Seyffarth [2] as follows:

$$\alpha_\gamma - \alpha_{\mathrm{P}} = \alpha^{\mathrm{E}} = -\frac{2p\,(a_1-a_2)^2}{R^2T}\ \frac{\Delta\gamma}{\Delta T} \qquad \ldots \quad (3)$$

where a_1 and a_2 are Van der Waals coefficients involved in the chemical excess potential.

As the mole fractions can be determined experimentally, one can measure the thermal diffusion factor α_γ given by Eq. (1) without any difficulty.

On the other hand, when one wants to determine α_{P} according to Eq. (2) the question of measuring the partial pressure differences arises. This measurement is possible only in special cases.

We have chosen a hydrogen-carbondioxide mixture for our investigation using a two bulb apparatus. The partial pressure of carbondioxide in the cold bulb was determined with the aid of the vapour pressure curve as done by Dickel and Seyffarth [2]. In the hot bulb, the partial pressure of hydrogen was determined by palladium resistance measurements instead of calculating it using the real gas equation [2].

2. The Palladium Occlusion Method

The fact that the electrical resistance of palladium varies with its hydrogen content was known as early as 1869 and many measurements of the phenomenon have been made since [3, 4].

The high pressure two bulb apparatus used earlier by Dickel and Seyffarth [2] was modified to suit the new procedure by fabricating a new screw of the alloy VACON 10 having four electrically insulated leads. This was used in the hot bulb with special scalants to withstand high pressures. Two of the leads served to connect the ends of a palladium wire of 99.99 % purity, 0.1 mm diameter, 30 cms length to a precision Wheatstone Bridge (the palladium wire was supplied by M/s. W. C. Heraeus, Hanau). A platinum resistance thermometer was attached to the other two leads in order to measure the temperature of the gas in the hot compartment accurately. The two bulb apparatus and the accessories were assembled as described earlier [2].

For the various temperatures of the hot bulb, isotherms of the relative electrical resistance of loaded palladium R_{P}/R_0 (where R_{P} is the equilibrium resistance of the palladium wire after occlusion of hydrogen and R_0 the hydrogen free resistance at the required temperature) vs. the pressure of hydrogen gas were experimentally determined. These have been plotted in Figure 1.

The palladium wire was replaced after each experiment by a new one from the same lot. Thus the curves represent the limiting change in resistance of palladium wire while loading it with hydrogen at different temperatures.

---

* Present address: Bhabha Atomic Research Centre, Engineering Hall No. 5, Bombay - 85.

Reprint requests to Prof. Dr. G. Dickel, Physikalisch-Chemisches Institut der Universität *D-8000 München 2*, Sophienstr. 11.

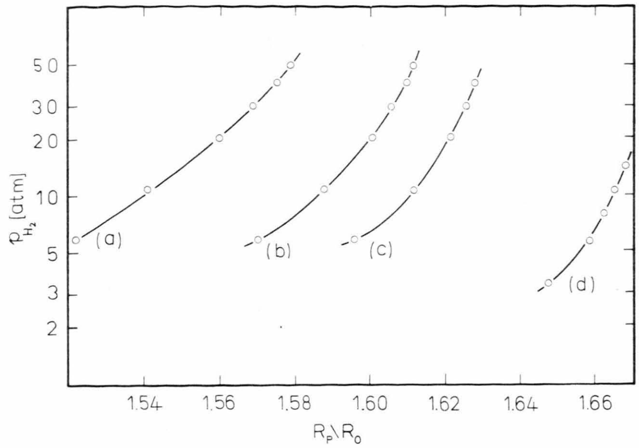

Fig. 1. Values of R_p/R_o of palladium wire vs. pressure of hydrogen gas. Curve (a): 90° C; Curve (b): 80° C; Curve (c): 70° C; Curve (d): 50° C.

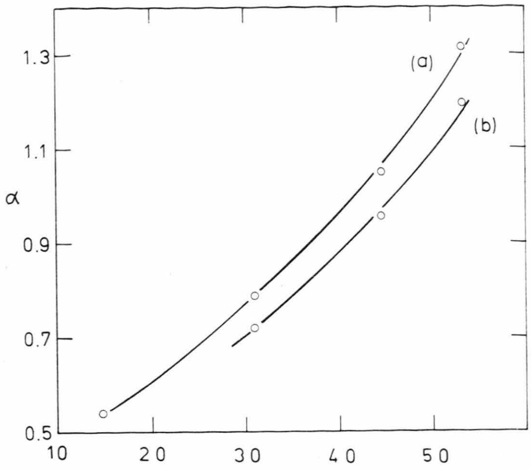

Fig. 2. Thermal diffusion factor of $H_2 - CO_2$ vs. total pressure of the gas mixture.
Curve (a): Values of α_y; Curve (b): Values of α_p.

3. Measurements

a) *Partial Pressures*

The temperature of the bottom bulb was so chosen that the carbondioxide remained in equilibrium with a small quantity of its liquid throughout the experiment. This helped us to determine the partial pressure of carbondioxide in the bottom compartment as the same was given by the vapour pressure at that temperature. The temperature difference between hot and cold bulbs was kept constant at a value of 100 °C in all cases. After the attainment of equilibrium the change in relative electrical resistance of the palladium wire was measured. The unknown partial pressure of hydrogen in the hot bulb was found by interpolation of the corresponding isothermals. The resistance measurements had an accuracy of 0.1 %.

b) *Mole Fractions*

Small quantities of gases were removed from the top and bottom of the two bulb apparatus after each experiment and analysed using a Mass Spectrometer. The mole fractions were determined with the help of a calibration curve involving an experimental error of 2 %.

4. Results

The values of the temperature of the cold bulb (T), the total pressure (p), the mole fractions and the partial pressures of carbondioxide in the bottom and top bulbs have been given in Table I. Also, the values of the thermal diffusion factor α_y obtained from the mole fractions and α_p obtained from the partial pressures have been included in the above Table. α^E has been calculated using Equation (3). The values of a_1 and a_2 were taken from standard tables [5] and they are: $a\,(CO_2) = 3.6$ l^2 atm./mole^2; $a\,(H_2) = 0.244$ l^2 atm./mole^2. The differences between α_y and α_p have also been plotted in Figure 2. The experimental error involved in the partial pressure measurement in experiment No. 1 was quite large due to the insensitive nature of the palladium resistance isothermal and therefore, the corresponding point could be ignored in the graph. The maximum experimental error involved in the measurement of α_p was estimated to be 10 %.

Table 1. Values of Thermal Diffusion Factor of Hydrogen Carbondioxyde.

No.	T °K	$\Delta T / T$	P atm.	γ_{CO_2} bottom	γ_{CO_2} top	α_y	p_{CO_2} bottom atm.	p_{CO_2} top atm.	α_p	$\alpha_{\exp}^E$	α^E
1	223	0.448	14.8	0.54	0.48	0.539	8.0	6.8	0.729	—0.190	0.025
2	245	0.412	31.0	0.56	0.48	0.789	15.5	13.2	0.721	0.068	0.060
3	252	0.397	44.6	0.60	0.50	1.050	24.3	20.1	0.957	0.093	0.102
4	263	0.380	53.3	0.60	0.48	1.315	29.3	23.3	1.197	0.118	0.142

5. Discussion

The idea that the pressure dependence of the thermal diffusion factor is a property of the real nature of the gases was proposed by Becker [6]. Haase [7] has tried by a plausible phenomenological consideration to separate from the usual thermal diffusion factor a thermodynamical part which contained the pressure dependence caused by the properties of a real gas. This part is evidently included in α^E given by Equation (3). We are convinced that the idea to regard the partial pressure differences instead of the concentration differences as the forces of thermal diffusion flux and the subsequent distinction between α_p and α_γ gives a more convenient representation of the physical phenomenon. The agreement between the values of $\alpha_{exp}{}^E$ and α^E in the high pressure range within the experimental error seems to have proved the above statement.

Acknowledgements

We thank Mr. R. Kretner for interesting discussions throughout this work. Also, our thanks are due to the authorities of I.A.E.A., Vienna and the Bundesministerium für Bildung und Wissenschaft for financial assistance to one of the authors (T.K.S.N.) and to the Fonds der Chemischen Industrie for means to buy the necessary equipment.

---

[1] G. Dickel, Z. Phys. Chem. N. F. **33**, 337 [1962].

[2] G. Dickel and K. Seyffarth, Z. Phys. Chem. N. F. **59**, 63 [1968].

[3] D. P. Smith, Hydrogen in Metals, The University of Chicago Press, Chicago 1937.

[4] F. A. Lewis, The Palladium Hydrogen System, Academic Press, London 1967.

[5] Handbook of Chemistry and Physics, Chemical Rubber Publishing Co. 1963.

[6a] E. W. Becker and A. Schulzeff, Naturwiss. **35**, 218 [1948].

[6b] E. W. Becker, Z. Naturforsch. **5a**, 457 [1950].

[6c] E. W. Becker, J. Chem. Phys. **19**, 131 [1951].

[7a] R. Haase, Z. Phys. **127**, 1 [1949].

[7b] R. Haase, Z. Phys. Chem. **A 196**, 219 [1950].

[7c] R. Haase, Z. Elektrochem., **54**, 450 [1950].