Water Limitation in the C-H-O System Over Iron

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Carbon dioxide and hydrogen will react over iron at 800° to 1 000°K and 1 bar pressure yielding water, carbon monoxide, methane, and carbon. In addition, iron oxides and carbides form during reaction. Phase diagrams are used to analyze this complex reaction system. Data are presented which suggest that the formation of magnetite (Fe_3O_4) or wustite (Fe_xO) inhibits carbon formation. The water yield thus observed is limited by the time dependent iron-iron oxide-gas equilibrium. Preliminary data also suggest that the formation of carbides has little effect on water yield.

SCOPE

In the temperature range 800 to 900 K and 1 bar pressure, iron will catalyze the reaction of hydrogen and carbon dioxide to produce carbon monoxide, water, methane, and carbon. However, the predicted equilibrium water concentration is never achieved even after long residence times. The work of Walker et al. (1959) and Ruston et al. (1969) have shown that iron oxides and carbides form under these conditions. The formation of these solid iron phases can affect the catalytic properties of the iron and in so doing affect the observed water yield.

In such complex systems, gas phase reactions can be catalyzed differently by solid phases formed during reaction. To analyze this system, phase diagrams were used to characterize the solid surface phase(s). Through the use of phase diagrams, the chemical potentials (gas phase composition) were set to favor the solid phase(s) of interest. Gravimetric analysis and chromatographic evaluation of reactor effluent allowed the determination of the catalytic properties of the various phases.

CONCLUSIONS AND SIGNIFICANCE

When a gas mixture of carbon dioxide, carbon monoxide, water, hydrogen, and methane is exposed to an iron catalyst, carbon deposition will cease if the catalyst is oxidized. Thus there exist critical values of the ratios P_{CO}/P_{CO_2} and P_{H_2}/P_{H_2O} below which carbon deposition will not occur. Experimental data indicate that the hydrogen-water equilibria is the more important; that is, even if the P_{CO}/P_{CO_2} ratio is such that reduced iron is favored, carbon will not deposit if the P_{H_2}/P_{H_2O} ratio is less than the equilibrium value for oxide formation. Although little is known about the formation and decomposition of iron carbides under these conditions, initial experiments indicate they are of secondary importance in determining water yield. Maximum water production is determined by the iron oxide/α-iron equilibrium, not by the graphite-gas equilibrium.

Closed life support systems must incorporate some scheme to recover the recycle oxygen from metabolic carbon dioxide. Deep space manned missions and long range submarines would be examples of such systems.

As carbon dioxide is a very stable molecule, oxygen is normally recovered in a two-step process. Reduction is first accomplished with hydrogen, and the product water is subsequently electrolyzed. If the reduction is carried out over a nickel or ruthenium catalyst at low temperature, water and methane are the principal products. Disposal of the methane may be a serious problem, and the loss of four atoms of hydrogen for each molecule of carbon dioxide reduced requires some form of hydrogen resupply. If, however, the reaction temperature is raised to 800 to 900 K and an iron catalyst used, solid carbon is deposited. Water, carbon monoxide, and methane are the principal product gases. When this latter process is operated in a recycle mode with water removal, the net result can be expressed as

$$2H_2 + CO_2 = 2H_2O + C \qquad (1)$$

With the electrolysis step

$$2H_2O = 2H_2 + O_2 \qquad (2)$$

the overall reaction is

$$CO_2 = O_2 + C \qquad (3)$$

Reaction (1) has often been called the Bosch reaction.

In prototype Bosch reactors operated by NASA, even at long residence times, the measured product water has always been far less than that predicted for an equilibrium system containing methane, carbon monoxide, carbon dioxide, hydrogen, water, and carbon. The study described in the present paper was undertaken primarily to ascertain the reason for this low water yield.

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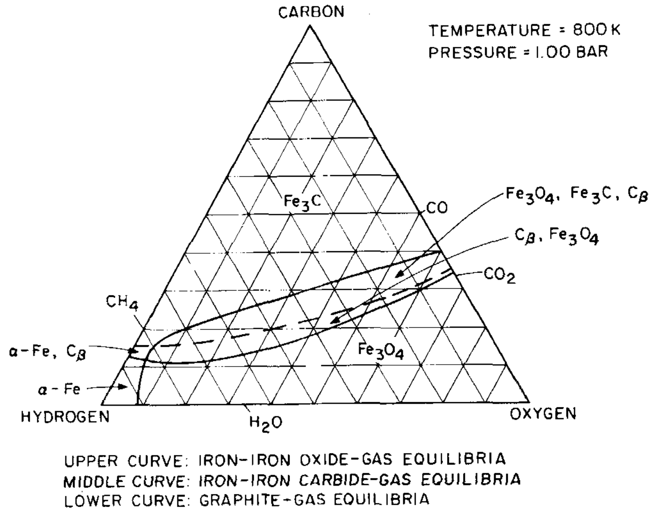

Figure 1. Typical phase diagram.

REACTION DYNAMICS

In the Bosch reactor, carbon may be formed by reactions (4) and (5)

$$2CO = CO_2 + C \qquad (4)$$

$$H_2 + CO = H_2O + C \qquad (5)$$

and the gaseous components are subject to the reverse water-gas shift reaction (5)-(4):

$$H_2 + CO_2 = H_2O + CO \qquad (6)$$

Methane formation may be included as, for example

$$2H_2 + C = CH_4 \qquad (7)$$

In addition to the reactions shown above, the iron catalyst may also play a role as a reactant. Ruston et al. (1969) have shown that iron carbides may form in addition to carbon. Walker et al. (1959) and Manning and Reid (1977) discuss the formation of iron oxides when the fraction of carbon dioxide in the gas favors this reaction. These studies are important in the present context since neither iron carbides nor iron oxides are believed to be good catalysts for the Bosch reaction; that is, the selectivity of the catalyst seems to depend strongly on the chemical and physical state of the iron.

To quantify equilibrium states in the Bosch reaction system, the phase diagram approach of Tevebaugh and Cairns (1964) is advantageous. Manning and Reid (1977) suggested this method to study the iron-iron oxide system. An extension to include the three pertinent equilibria, carbon (graphite)-gas, iron-iron oxide-gas, and iron-iron carbide-gas, is shown in Figure 1 at 800 K and 1 bar total pressure. The composition of any gas mixture composed of hydrogen, oxygen, and carbon may then be represented. The top curve, which shows a sharp change in slope near the hydrogen apex, represents the phase boundary for the iron-iron oxide transition between α-iron and magnetite (Fe_3O_4). The middle (dashed) curve represents the metastable iron-iron carbide transition. Equilibrium considerations suggest that the carbide is cementite (Fe_3C), but even this carbide is thermodynamically unstable relative to iron and carbon. Rates of formation and decomposition may, however, be such as to necessitate inclusion of this solid phase. The lowest curve, which is concave up, indicates the equilibrium between carbon (graphite) and gas.

Diagrams as exemplified by Figure 1 were employed in this study to delineate regions where carbon would be expected to be deposited. If positive weight gains were noted, it was inferred that the equilibrium state of the iron present was such as to insure its catalytic activity. Analysis of reactor effluent was used to verify that the weight gain was due to carbon deposition and, in addition, to indicate the catalytic effects of the solid iron phase for reactions (6) and (7).

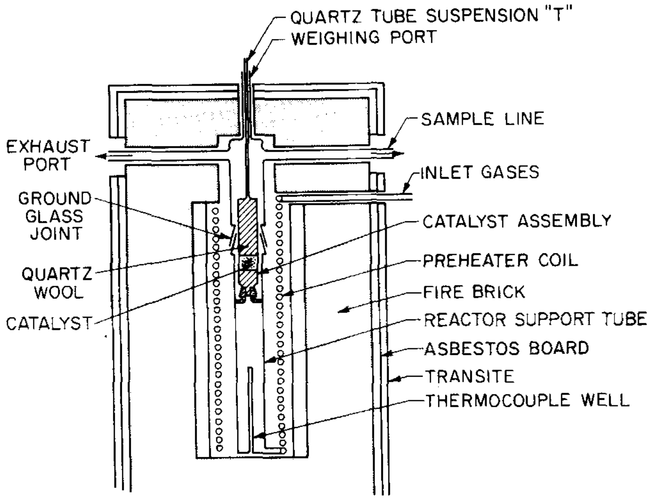

Figure 2. Reactor assembly in furnace.

EXPERIMENTAL

The experimental equipment and operational procedures were similar to those used by Manning and Reid (1977). The reactor is shown in Figure 2. The feed gases, which were individually metered and mixed upstream, were passed into the bottom of a 28 mm diameter vertical quartz tube. Two thermocouples were set in a thermowell under the catalyst bed. One was employed to yield a continuous reading of the inlet gas temperature, while the output from the other was fed to a proportional controller that maintained the bed temperature at a preselected value. The catalyst assembly was positioned midway in the quartz tube. Number 2 steel wood was used as a catalyst, and, normally, about 500 mg were charged. The composition of the catalyst is shown in Table 1. During a run, the reacting gases passed through the catalyst, but, at intervals of 5 to 10 min, the gas flow was diverted and the catalyst carrier weighed *in situ* with an analytical balance. Weight changes of ±1 mg could readily be detected.

The inlet and outlet gas streams were sampled and analyzed using an on-line chromatograph. An external standard was used in conjunction with the method of Dal Nogare and Juvet (1962) to obtain all gas compositions except hydrogen. The latter was determined from an empirical calibration following the method of Purcell and Ettre (1965).

The reaction pressure was maintained at about 1 bar, and the total reactant gas flow rate was 20 cm^3/s (STP). Temperature varied between 800 to 900 K. Prior to almost all experiments, the catalyst was pretreated to increase surface area. Pretreatment consisted of oxidizing the catalyst with carbon dioxide and water, followed by reduction in pure hydrogen. This proceeding was carried out at 900 K and resulted in an increase in surface area from 389 cm^2/g for untreated catalyst to 1 912 cm^2/g for the conditioned catalyst (Sacco, 1977).

TABLE 1. CATALYST COMPOSITION

Element	Wt %
Fe	98.882
Mn	0.700
C	0.360
P	0.040
S	0.018
N	0.400 ppm

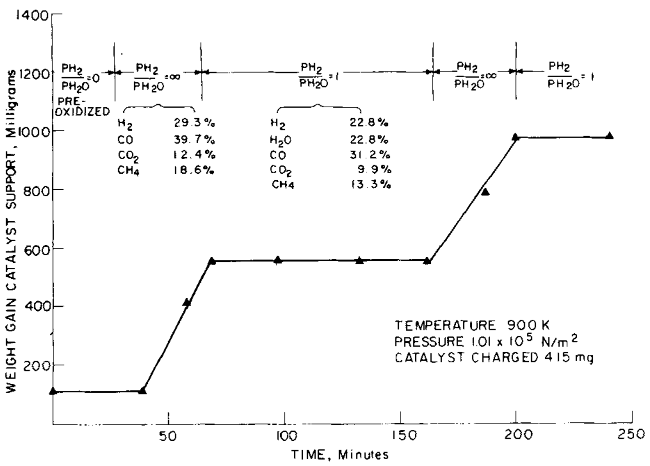

Figure 3. Control of carbon deposition through variation in P_{H_2}/P_{H_2O} ratio.

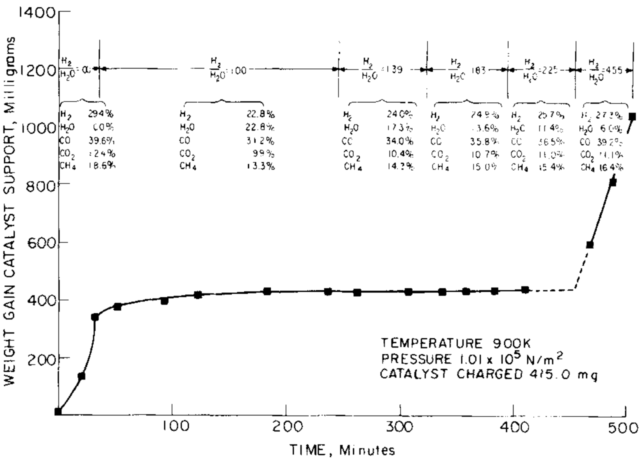

Figure 4. Carbon inhibition as a function of P_{H_2}/P_{H_2O} ratio.

OXIDATION STUDIES OF THE IRON CATALYST

Oxidation in a Bosch reactor may be controlled by either the P_{H_2}/P_{H_2O} ratio or the P_{CO}/P_{CO_2} ratio. These ratios control the surface conditions through reactions (8) and (9):

$$yH_2 + Fe_xO_y = xFe + yH_2O \tag{8}$$

$$yCO + Fe_xO_y = xFe + yCO_2 \tag{9}$$

Within the temperature range of interest in the Bosch reactor, there are two distinctly different iron oxide phases in equilibrium with α-iron. Below 833 to 843 K, magnetite (Fe_3O_4) is the stable iron oxide. Above 833 to 843 K, wustite (Fe_xO) is the oxide phase expected. Thus, the effects of both these oxides on the carbon deposition rate was of interest. In addition, the sensitivity of the catalyst to adjustments in the P_{H_2}/P_{H_2O} ratio and P_{CO}/P_{CO_2} ratio was explored.

Initial experiments were run to determine if iron oxide did inhibit carbon deposition. The experiments were planned so that a determination could also be made as to the controlling oxidation reactions. Figures 3 and 4 are representative of what was observed.

In Figure 3, 415 mg of steel wool catalyst were initially oxidized in a flowing stream of 77.2% carbon dioxide and 22.8% water at 900 K and 1 bar total pressure.

The P_{H_2}/P_{H_2O} ratio was then alternated between a value of ∞ (that is, no water) and a value of 1. The remaining gas phase compositions were set (from data generated from the phase diagrams) so that reaction (4) would proceed to the right, depositing carbon, while reaction (9) should proceed to the right reducing the surface. However, at a P_{H_2}/P_{H_2O} ratio 1, reaction (8) should proceed to the left, oxidizing the surface. Therefore, depending on the relative kinetic rates of reactions (8) and (9), if carbon deposition is inhibited, reaction (8) must control the surface condition.

As shown in Figure 3, carbon deposition is inhibited by oxide formation. In addition, it appears that the P_{H_2}/P_{H_2O} ratio [reaction (8)] may be more important than the P_{CO}/P_{CO_2} ratio [reaction (9)] in determining the surface conditions. Figure 3 indicates that reaction (4) is inhibited from depositing carbon by oxide formation. Figure 4 represents an experiment run to determine if reaction (5) is similarly inhibited.

In Figure 4, a P_{H_2}/P_{H_2O} ratio (∞) was used initially to deposit approximately 350 mg of carbon on 415 mg of steel wool catalyst. The reactor temperature was set at 900 K, and total pressure was 1 bar. As illustrated in Figure 4, no appreciable weight gain was noticed with P_{H_2}/P_{H_2O} ratios between 1.00 to 2.25. Upon changing the P_{H_2}/P_{H_2O} ratio to 4.55, rapid carbon deposition was observed. At all P_{H_2}/P_{H_2O} ratios greater than 1, the $P_{H_2O}/P_{H_2}P_{CO}$ ratios were such as to thermodynamically favor carbon deposition by reaction (5). Only when the P_{H_2}/P_{H_2O} ratio exceeded the equilibrium P_{H_2}/P_{H_2O} ratio for reaction (8) (2.75) did carbon deposition occur. The gentle rising slope in Figure 4 is attributed to slow surface oxidation.

Thus our results indicate that oxide formation (Fe_xO) inhibits deposition from both reactions (4) and (5). Also, once again, the surface appears to be controlled by reaction (8).

It was noted earlier that, at 900 K, the equilibrium iron oxide is wustite, Fe_xO. To study further the oxide inhibition reaction, a phase diagram similar to Figure 1 was developed at 900 K. This is shown in Figure 5. The lower curve on the right-hand side is the predicted phase boundary for β-graphite equilibrium. Gas compositions which fall above this curve would be predicted to deposit carbon. The upper curve which crosses the β-graphite phase curve is calculated from Gibbs energy data on wustite (Stull, 1965) at 900 K. Gas compositions lying above this curve should lead to a reduced iron phase, whereas those below would lead to an oxidized surface. Thus, our theory would predict no carbon deposition for compositions below the Fe_xO/α-Fe curve. The region between the two curves was one where one

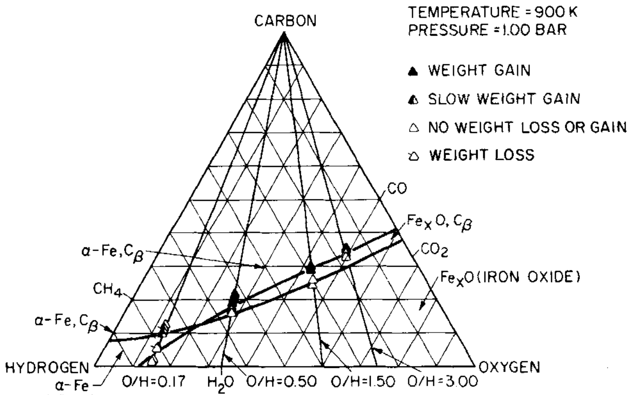

Figure 5. Determination of the iron/wustite phase boundary in a five component gas mixture at various oxygen/hydrogen ratios.

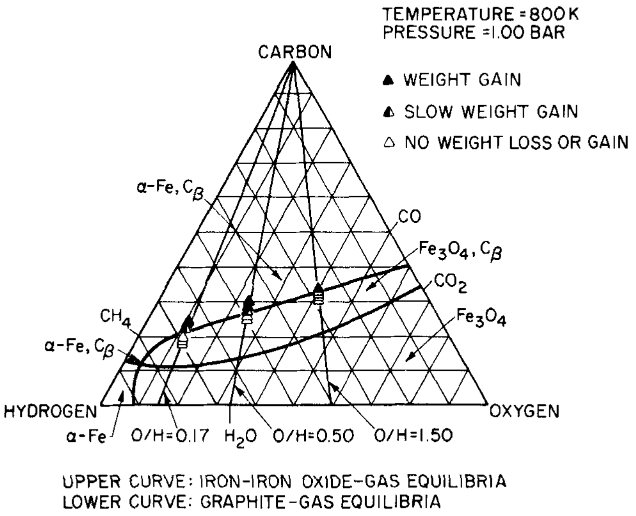

Figure 6. Inhibition of carbon deposition by Fe_3O_4 at various oxygen/hydrogen ratios.

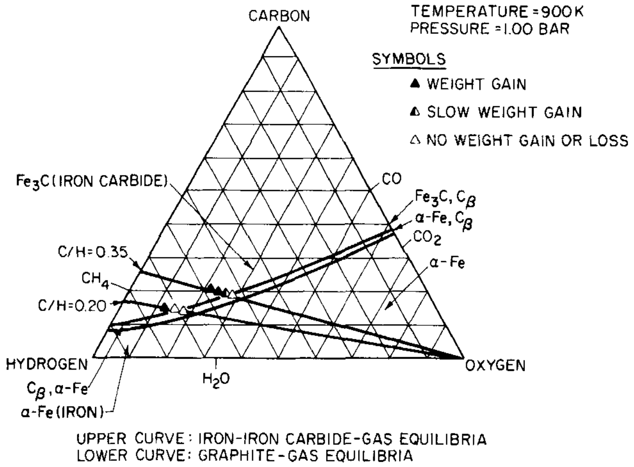

Figure 7. Determination of the iron/iron carbide phase boundary in a five component gas mixture at various carbon/hydrogen ratios.

could not predict *a priori* whether carbon would or would not be deposited. To study this region, five component (carbon monoxide, carbon dioxide, hydrogen, water, and methane) gas mixtures were prepared, but these were subdivided so that for any sequence of experiments, the oxygen/hydrogen ratio was held constant. As shown in Figure 5, except for some erratic results at the lowest oxygen/hydrogen value (the case where the fraction of water was the highest and condensation upon the quartz suspension bar was observed), the results support the contention that in the region between the β-graphite and wustite curves, carbon formation is not favored; that is, the iron oxide is not an effective catalyst.

The scatter of the data, when viewed on an expanded phase diagram, appeared somewhat in excess of what would have been expected from a propagation of error analysis. To determine if other factors were of importance, a separate study was conducted to determine if there may be transient structural changes playing a part in the observed results. The results from this study (Sacco, 1977) indeed show that multiple iron oxide phases form at 900 K and the system response time was significantly affected by transient changes between the oxides.

Figure 5 was drawn for experiments carried out at 900 K; similar experiments were also made at 800 K, where the stable iron oxide is magnetite. The results are presented in Figure 6. Each set of test runs was made at a constant oxygen/hydrogen gas ratio, but the overall composition varied to obtain compositions which would lie along the oxygen/hydrogen locus lines. Without exception, it was found that if the gas composition were such as to lie above the $Fe_3O_4/\alpha\text{-}Fe$ phase boundary, carbon was deposited. Below this boundary, where magnetite formed, carbon deposition ceased.

THE EFFECT OF CARBIDE ON CARBON DEPOSITION

The role of carbides during carbon deposition is still not clear. The problem lies in the fact that carbides are difficult to identify and can form not only during reaction but during the reactor cooldown.

In an attempt to determine the effect of carbides on carbon deposition, two runs were performed at fixed carbon/hydrogen values of 0.20 and 0.35, respectively. The catalyst was preconditioned using the standard procedure and a carbon bed laid down.

Figure 7 indicates that a weight gain was observed in the region where cementite (Fe_3C) would be expected to be the stable solid phase. However, the effluent in both runs showed no change in methane concentration; the observed weight gain resulted from carbon monoxide conversion.

There are two possible reactions which could account for the weight gain observed, reaction (10) and/or reaction (4):

$$2CO + 3Fe = Fe_3C + CO_2 \qquad (10)$$

$$2CO = CO_2 + C \qquad (4)$$

From stoichiometric considerations, it is impossible to determine which reaction accounts for the observed weight gain. The fact that 3.5 times as much weight gain is observed as needed for complete carbiding (35 mg) indicates that the weight gain is probably due to carbon deposition. This is in agreement with the work of Podgurski et al. (1950) and Walker et al. (1959) who suggest that carbiding with carbon monoxide is very slow.

Although the data are inconclusive in determining if carbides inhibit or catalyze carbon deposition, from an operational standpoint, it appears that oxide formation is the most immediate problem in efficient Bosch reactor operation. That is, the iron-iron oxide gas phase boundary represents the time dependent "equilibrium" composition one could realistically expect to achieve.

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Drag Coefficient and Relative Velocity in Bubbly, Droplet or Particulate Flows

Drag coefficient and relative motion correlations for dispersed two-phase flows of bubbles, drops, and particles were developed from simple similarity criteria and a mixture viscosity model. The results are compared with a number of experimental data, and satisfactory agreements are obtained at wide ranges of the particle concentration and Reynolds number. Characteristic differences between fluid particle systems and solid particle systems at higher Reynolds numbers or at higher concentration regimes were successfully predicted by the model. Results showed that the drag law in various dispersed two-phase flows could be put on a general and unified base by the present method.

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SCOPE

The ability to predict the interfacial drag or the relative velocity between phases is of considerable importance for analyzing a dispersed two-phase system under steady state or transient conditions. For example, the designs and performances of fluidization, sedimentation, and extraction systems as well as various heat transfer systems can be significantly affected by a reliable interfacial drag correlation.

A number of correlations for the relative velocity could be found in the literature. However, most of them are developed from a limited number of experimental data, and, therefore, are applicable only to a certain type of dispersed flows. In the past, different empirical or semi-empirical correlations had been obtained for solid and fluid particle systems at different Reynolds numbers and particle sizes.

The purpose of this article is to develop constitutive relations for the drag force and the relative velocity for bubbly, droplet, and particulate flows by a unified method. Simple drag similarity criteria and mixture viscosity model are introduced in the analysis. Present drag and relative velocity correlations cover all concentration ranges and wide Reynolds number ranges, from the Stokes regime up to the Newton's regime, or the churn-turbulent flow regime. This unified and consistent model gives an improved understanding of the mechanisms of interfacial momentum transfer in dispersed two-phase flows. It can be useful for predicting void fractions, interfacial area, particle residence time, and occurrences of flooding or concentration shock waves.

CONCLUSIONS AND SIGNIFICANCE

It has been shown that the present drag similarity criteria based on the mixture viscosity concept can be successfully applied to develop a relative velocity correlation for bubbly, droplet, and particulate flows. Comparing theoretical predictions to over 1,000 experimental data indicated that satisfactory agreements could be obtained at wide ranges of particle concentration and Reynolds number. For spherical solid particle systems, the data from the Stokes regime up to the Newton's regime within the concentration range of 0 to 0.55 are examined, whereas for fluid particle systems, the distorted particle and churn-turbulent regimes are extensively studied, because of their practical importance. The success of the present correlation at up to the highest concentration range for spherical solid particle systems was accomplished by introducing the maximum packing in the mixture viscosity relation. This was a definite improvement over the existing correlations.

It is also noted that the present model is sufficient up to the foam or dense packing regime, with the concentration ranging from 0.5 to 0.95 for both bubbly and droplet flows. These comparisons indicated that the postulated drag similarity law based on the mixture viscosity concept was appropriate. Therefore, the drag law governing the motions of bubbles, drops and particles in various dispersed two-phase flows can be explained by a unified and consistent model developed here.

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