

weight percent basis for concentrations below 10% acetone (9). Therefore, the driving force for transfer into or out of the jet for a given concentration of acetone in one of the phases is approximately the same. The concentration of 5% by weight acetone was used. The interfacial tension was reduced from 31.2 dynes/cm. for benzene-water to 20.2 dynes/cm. when the benzene and water each contained 5% by weight acetone at equilibrium.

The drop volume was smaller for the mass transfer systems than for the saturated benzene-water system. Equation (30) predicted the drop volumes for mass transfer when the equilibrium interfacial tension for 5% by weight acetone in each phase was used. These results indicate that for this system the effective interfacial tension was equal to the equilibrium interfacial tension over the velocity range investigated. The subject of effective interfacial tension has been extensively studied (1 to 3), and it has been shown that the main variables are the rate of surface renewal and the solute molecular size. It appears that the acetone molecule was small enough that its diffusion rate was sufficient to maintain the equilibrium interfacial tension.

Therefore, if the solute is of small molecular size and its concentration is low, Equation (30) can be applied to mass transfer systems if the equilibrium interfacial tension is used. The equation predicts only the drop size leaving the nozzle, and it does not include coalescence effects in the continuous phase above the nozzle.

NOTATION

A	= cross-sectional area of nozzle, sq. cm.
a	= exponent as defined by Equation (26)
C_D	= drag coefficient
D_F	= diameter of detached drop, cm.
D_{FS}	= diameter of attached drop at instant forces are in balance, cm.
D_N	= nozzle inside diameter, cm.
F	= Harkins-Brown correction factor
F_B	= buoyant force, dynes
F_D	= drag force, dynes
F_K	= kinetic force, dynes
F_S	= interfacial tension force, dynes
g	= acceleration of gravity, 980 cm./sec. ²
h	= distance from nozzle tip to leading edge of drop, cm.
h_o	= diameter of liquid left on nozzle after drop break off, cm.
K	= numerical coefficient in several equations
m	= mass of drop, g.
n	= exponent in Equation (17)

Q	= volume flow rate of dispersed phase, cc./sec.
R	= radius of neck of drop, cm.
R_N	= nozzle radius, cm.
t	= time, sec.
t'	= dimensionless time, defined by Equation (23b)
t_B	= time duration of drop necking, sec.
t_F	= time required for forces to reach equilibrium, sec.
U_F	= velocity of the forming drop at the instant necking starts, cm./sec.
U_N	= dispersed phase average velocity through the nozzle, cm./sec.
U_R	= radial necking velocity, cm./sec.
U_R'	= dimensionless radial necking velocity
U_V	= vertical rise velocity during necking, cm./sec.
U_V'	= dimensionless vertical rise velocity during necking, as defined by Equation (23a)
U_Z	= local dispersed phase velocity in the nozzle, cm./sec.
V_F	= drop volume after break off from the nozzle, cc.
V_{FS}	= liquid volume attached to the nozzle when necking starts, cc.
V_{FN}	= volumetric flow out of the nozzle during necking, cc.
μ	= continuous phase viscosity, g./ (cm.) (sec.)
ρ, ρ'	= densities of continuous and dispersed phases, respectively, g./cc.
σ	= interfacial tension, dyne/cm.

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Part II. Prediction of Jetting Velocity

Equations are derived for predicting the velocity above which a jet forms when one Newtonian liquid is injected into a second stationary immiscible liquid. Comparison of the theory with experimental data obtained for fifteen liquid-liquid systems and five nozzle diameters shows a mean error of 6.6%. The equation also predicts the jetting velocity for injection of liquids into gases and the critical velocity at which bubble formation changes from a constant volume to a constant frequency mechanism for gas injection into liquids.

The drop volume correlation developed in Part I applies only at low velocities where drops form directly at the nozzle. As the flow rate through the nozzle is increased, a critical velocity called the *jetting velocity* is reached, above which a jet of liquid issues from the nozzle. The

jet breaks into drops, but, because the drop formation mechanism has changed, the drop size can no longer be predicted by the low velocity correlation. To define the region of applicability of the low velocity drop volume equation, it is necessary to predict the jetting velocity.

Smith and Moss (7) found that for liquids injected into gases the jetting velocity U_J was given by

$$U_J = K \left(\frac{\sigma}{\rho' D_N} \right)^{1/2} \quad (1)$$

where K was between 2.0 and 3.0. Tyler and Richardson (8), working also with liquids injected into gases, found that Equation (1) predicted the jetting velocity, and that K was between 2.3 and 3.0. Both pairs of investigators found that K depended mainly on the surface tension, the lowest values of K corresponding to the lowest surface tensions.

Hayworth and Treybal (3) worked with liquid-liquid systems and found that jets usually formed when the velocity through the nozzle became 10 cm./sec. This was an average value for their systems, and no attempt was made to define the jetting velocity more precisely.

Fujinawa et al. (1) found that the jetting velocity for liquid-liquid systems could be correlated by

$$U_J = 4.4 \sigma^{0.20} / D_N^{1/2} \quad (2)$$

Shiffler (6) developed a correlation for the lower critical Weber number at which a sharp increase in surface area is observed in liquid-liquid systems. Since the increase in surface area generally corresponds to jet formation, Shiffler's analysis can alternatively be considered a correlation of the Weber number at the jetting velocity. Shiffler found that the Weber number of jetting, defined as

$$N_{We} = U_J \left(\frac{\rho' D_N}{\sigma} \right)^{1/2} \quad (3)$$

was a unique function of a system length parameter, defined by

$$D_N / l_s = D_N (g \Delta \rho)^{1/2} / (\pi \sigma)^{1/2} \quad (4)$$

Both liquid-liquid correlations are empirical and give little insight into the mechanism of jet formation. This paper presents a theoretical analysis for predicting the jetting velocity which shows good agreement with experimental data.

THEORY

There are two possible jet formation mechanisms on which a prediction of the jetting velocity can be based.

The first mechanism considers that a jet will form if there is sufficient upward force at the nozzle exit to form a jet. If a drop is not large enough to detach from the nozzle, the kinetic force of the liquid leaving the nozzle can either enlarge the drop or raise the drop up on a cylinder of liquid, thus forming a jet. It is postulated that if sufficient upward force exists to form a jet, this will occur in preference to further enlargement of the drop.

Consider conditions at the nozzle tip immediately following detachment of a drop of diameter D_F . To form a jet the net upward force at the nozzle tip must overcome the interfacial tension force

$$F_S = \pi \sigma D_N \quad (5)$$

The upward forces consist of the kinetic force F_K of the fluid exiting from the nozzle, given by

$$F_K = \pi \rho' U_N^2 D_N^2 / 3 \quad (6)$$

for a dispersed phase having a parabolic velocity distribution, and a force F_P arising from the pressure difference between the dispersed and continuous phases. The pressure p' of the liquid leaving the nozzle must be greater than the pressure p in the continuous phase by the amount

$$p' - p = 4\sigma / D_F \quad (7)$$

which is the excess pressure necessary to sustain a spherical drop. The excess pressure force is

$$F_P = \pi \sigma D_N^2 / D_F \quad (8)$$

At the jetting velocity

$$F_K + F_P = F_S \quad (9)$$

Substitution of Equations (5), (6), and (8) into Equation (9) and rearrangement yield

$$U_J = 1.73 \left[\frac{\sigma}{\rho' D_N} \left(1 - \frac{D_N}{D_F} \right) \right]^{1/2} \quad (10)$$

where U_J , the jetting velocity, is the nozzle velocity at which a jet first forms, and D_F is the diameter of the drop which would form at the nozzle velocity U_J if a jet did not form.

For a flat velocity profile in the dispersed phase

$$F_K = \pi \rho' U_N^2 D_N^2 / 4 \quad (11)$$

and the jetting velocity becomes

$$U_J = 2.0 \left[\frac{\sigma}{\rho' D_N} \left(1 - \frac{D_N}{D_F} \right) \right]^{1/2} \quad (12)$$

The second mechanism considers that a jet will form when the initial rise velocity of a drop is sufficiently low that the drop will rise less than one drop diameter during the time of formation of the next drop. The drops will then merge to form a continuous jet. Although high-speed movies of drop formation at velocities just prior to jetting show no evidence that such a mechanism was operative for any of the systems studied in Part I, Kintner (4) has observed this phenomenon for the injection of benzyl alcohol downward into water.

If the drops are of uniform size and spherical, a detached drop must rise at least one drop diameter during the time of formation of the subsequent drop to escape from the nozzle. Actual drops are deformed to some extent, but the effects of deformation tend to cancel because the attached drop is elongated in the axial direction while the free drop tends to be flattened owing to drag resistance.

If the time for the drop to rise one drop diameter is compared with the drop formation time, the condition for which the drops will merge is

$$\frac{D_F}{U_{Ri}} > \frac{V_F}{Q} \quad (13)$$

where U_{Ri} is the average rise velocity for the first diameter of rise. The criterion for drop merging, expressed in terms of the jetting velocity, is

$$U_J = \frac{2D_F^2 U_{Ri}}{3D_N^2} \quad (14)$$

for spherical drops.

A prediction of the rise velocity is required in Equation (14). Most studies of the steady state rise velocity of drops have shown that the rise velocity increases with drop diameter up to a critical diameter above which the velocity becomes independent of diameter. Klee and Treybal (5) have obtained empirical equations for the two regions.

For small drops

$$U_{Ri} = 38.3 \rho^{-0.45} \Delta \rho^{0.58} D_F^{0.70} \mu^{-0.11} \quad (15)$$

and for large drops

$$U_{Ri} = 17.6 \rho^{-0.55} \Delta \rho^{0.28} \sigma^{0.18} \mu^{0.10} \quad (16)$$

TABLE 1. COMPARISON OF PREDICTED JETTING VELOCITIES WITH EXPERIMENTAL DATA

System No.	Nozzle diameter, cm.	U_J experimental, cm./sec.	U_J from Equation (10), cm./sec.	% error using Equation (10)	U_J from Equation (18), cm./sec.
1	0.0813	40.2	39.8	-1.0	212.0
1	0.160	25.9	25.8	-0.4	78.0
1	0.254	19.9	19.2	-3.5	53.5
1	0.332	16.4	15.6	-4.9	39.8
1	0.688	10.8	7.54	-30.2	17.4
2	0.0813	31.9	33.4	+4.7	150.0
2	0.254	18.6	16.7	-10.2	67.0
2	0.688	7.15	6.25	-12.6	21.2
3	0.0813	31.9	32.4	+1.6	98.8
4	0.0813	31.9	31.5	-1.3	92.2
5	0.0813	28.4	31.0	+9.1	68.8
5	0.254	14.2	14.2	0.0	40.8
6	0.0813	31.9	32.1	+0.6	113.2
6	0.254	14.2	14.0	-1.4	37.2
7	0.0813	6.61	6.67	+0.9	20.3
7	0.160	2.74	3.48	+27.0	9.76
8	0.0813	30.6	32.7	+8.5	297.0
8	0.254	17.6	17.8	+1.1	145.4
9	0.254	16.2	19.8	+22.2	86.2
10	0.254	18.25	20.4	+11.9	86.5
11	0.254	21.05	20.6	-2.1	81.0
12	0.254	22.05	20.1	-8.8	65.0
13	0.0813	31.7	32.2	+1.6	270.0
14	0.0813	25.8	25.9	+0.4	291.0
15	0.0813	25.8	25.9	+0.4	291.0

The critical diameter separating these two equations is given by

$$D_F = 0.33 \rho^{-0.14} \Delta \rho^{-0.43} \sigma^{0.24} \mu^{0.30} \quad (17)$$

The equations of Klee and Treybal were employed in Equation (14) to approximate U_{Ri} , because no reliable equations exist for the unsteady state rise velocity. Equation (14) then becomes

$$U_J = \frac{2D_F^2 U_{Ri}}{3D_N^2} \quad (18)$$

Both mechanisms of jet formation appear possible, and whichever mechanism gives the lower jetting velocity for a given system should be the controlling one. Equation (10), (12), or (18) can be combined with Equation (30) of Part I to predict the jetting velocity. The calculation is iterative because the drop diameter is a function of the nozzle velocity. A simplified computational procedure can generally be used. This procedure involves calculation of the drop diameter at static conditions using Equation (3) of Part I, calculation of the jetting velocity using the static drop diameter and Equation (10), (12), or (18), recalculation of the drop diameter using the estimated jetting velocity and Equation (30) of Part I, and finally recalculation of the jetting velocity using the revised drop diameter estimate. Further iterations are usually unnecessary.

RESULTS

Jetting velocities were measured by using the apparatus and liquid-liquid systems described in Part I. For all systems except heptane-glycerine, the jetting velocity was chosen to be the lowest experimental velocity at which a jet could be observed. In the heptane-glycerine system a normal appearing jet did not form when the 0.254- and 0.688-cm. nozzles were used, so the jetting velocity was chosen to be the velocity at which an observable change in the drop formation mechanism occurred. There is a

maximum uncertainty of about 10% in the experimental jetting velocities for most systems, because the rotameter scale prevented incremental velocity changes smaller than this amount to be read in the region near jetting.

A comparison of the experimental jetting velocities with those predicted by Equations (10) and (18) is presented in Table 1. Equation (10) was used for the theoretical predictions because the large length-to-diameter ratios of the nozzles assured fully developed laminar flow at the nozzle exit. The experimental drop diameters just prior to jetting were used in both theoretical equations because use of the experimental diameters provides a more realistic test of the jetting equation than use of drop diameters predicted by the correlation in Part I. The mean absolute error of 6.64% in predicting the jetting velocity from Equation (10) is not much greater than the 5% mean error present in the experimental determinations, and there are only three systems with errors significantly greater than the 10% maximum uncertainty in experimental jetting velocities. For all systems Equation (10) predicted a lower jetting velocity than Equation (18), consistent with the high-speed movies which showed no evidence of drop merging leading to jetting.

There are no experimental liquid-liquid data in the literature which can be used to test the jetting correlation, because not enough data points have been obtained to locate the jetting velocity accurately. For example, the data of Shiffler (6) often show a 100% change in velocity between the values immediately prior to and subsequent to jet formation. Although predicted jetting velocities fall in the proper interval between data points for all of Shiffler's systems, such agreement is not sufficient to confirm the analysis.

DISCUSSION

Equation (10) predicts the jetting velocity within 30% for all systems studied, but there are three system-nozzle combinations for which the discrepancy between theory and experiment is significantly greater than the maximum experimental uncertainty of 10% in the jetting velocity which arises from the inability to make smaller incremental changes in nozzle velocity.

The large error which exists in the heptane-water system (system 1) for the largest diameter nozzle is primarily a result of the inability to determine accurately from photographs the experimental onset of jetting. For the 0.688-cm. nozzle the transition to jetting was not as well defined experimentally as it was for smaller nozzles, and selection of the critical velocity at which a jet first forms was difficult. This difficulty was also evident in the heptane-glycerine runs (system 2) when the 0.688-cm. nozzle was used. For this reason, and also because drop deformation was quite large when the largest nozzle was used, this nozzle was not used for the other liquid-liquid systems.

The large percentage error in predicting jetting for the butyl alcohol-water system (system 7) when the 0.160-cm. diameter nozzle was used results in part from the low jetting velocity. Although the percentage error is large, the small absolute error of 0.7 cm./sec. suggests that the theory is valid for this system.

The one system for which the deviation between theory and experiment may be the result of a deficiency in the theoretical analysis is the paraffin oil-water one (system 9). The high dispersed phase viscosity caused earlier jetting than predicted, a fact consistent with the experimental observation that when a drop broke away from the nozzle the material was so cohesive that it tended to draw a jet of fluid out of the nozzle. This effect has not been considered in the present analysis.

Thus, the present analysis predicts jetting velocities which agree with experimental values within the limits of experimental accuracy for all systems except, possibly, those with a very high dispersed phase viscosity. The analysis is also an improvement over all previous predictive methods for liquid-liquid systems. The estimate of 10 cm./sec. given by Hayworth and Treybal (3) for the jetting velocity is an approximation which may be in error by more than 400%, as can be seen from the experimental jetting velocities in Table 1.

The correlation developed by Fujinawa et al. (1) shows the same jetting velocity-nozzle diameter dependence as Equations (10) and (12) when $D_N/D_F \ll 1.0$, but the interfacial tension dependence is different. A critical test of the Fujinawa correlation is provided by the butyl alcohol-water system (system 7) which has the low interfacial tension of 1.79 dynes/cm. The Fujinawa correlation predicts jetting velocities of 17.1 and 12.3 cm./sec. for the 0.0813- and 0.160-cm. diameter nozzles, respectively. The poor agreement between the predicted and experimental values suggests that the interfacial tension dependence is incorrect. The present analysis gives significantly better velocity predictions for the low interfacial tension system.

Comparison of the present analysis with Shiffler's correlation for the lower critical Weber number (6) is facilitated by a rearrangement of the results which Shiffler presented as a plot of lower critical Weber number vs. D_N/l_s . By transforming coordinates the plot forms a straight line whose equation is

$$\left(\frac{\pi N_{We}}{4}\right)^2 = 2.4 \left[1 - \left(\frac{D_N}{l_s}\right)^{0.78}\right] \quad (19)$$

Substituting the expressions for N_{We} and l_s given by Equations (3) and (4) into Equation (19) gives

$$\frac{U_j^2 \rho' D_N}{\sigma} = 3.89 \left[1 - \frac{0.410 D_N^{0.78} (g\Delta\rho)^{0.39}}{\sigma^{0.39}}\right] \quad (20)$$

This equation can be compared with Equation (12) which applies to flat velocity profiles which existed in Shiffler's experiments. Rearrangement of Equation (12) yields

$$\frac{U_j^2 \rho' D_N}{\sigma} = 4.0 \left(1 - \frac{D_N}{D_F}\right) \quad (21)$$

and substitution of the static drop volume given by Equation (3) of Part I for D_F gives

$$\frac{U_j^2 \rho' D_N}{\sigma} = 4.0 \left[1 - \frac{0.55 D_N^{2/3} (g\Delta\rho)^{1/3}}{\sigma^{1/3} F^{1/3}}\right] \quad (22)$$

The similarity between Equations (20) and (22) not only helps confirm the validity of Equation (12) for predicting jetting velocities when the dispersed phase has a flat velocity profile, but it also lends theoretical support to Shiffler's correlation.

There is nothing in the theoretical analysis which should limit the results to liquid-liquid systems, so a good test of the equations is their applicability to the injection of liquids into gases and to the injection of gases into liquids. The similarity of Equations (10) and (12) to the correlations developed by Smith and Moss (7) and Tyler and Richardson (8) for liquids injected into gases can be seen from Equation (1). The factor $(1 - D_N/D_F)^{1/2}$ is absent from the liquid-gas correlations, but since D_N/D_F was less than 0.10 in the experiments, the factor is sufficiently small that one would not expect it to appear in the correlations.

The difference in the numerical constant between the liquid-liquid and liquid-gas correlations is consistent with the fact that the liquid-gas equations do not predict the

jetting velocity as defined in the present study but rather the velocity above which the jet length becomes a linear function of nozzle velocity. For liquid-gas systems the jet length-velocity relationship does not become linear until the jet length reaches an L/D_N ratio of about 30, so the true jetting velocity is 20 to 30% lower than the critical velocity correlated. This fact is consistent with the lower coefficients obtained in the present analysis.

For gases injected into liquids jet formation is not observed experimentally. However, it has often been observed that while at low injection velocities the bubble volume is independent of velocity, at a critical velocity the mechanism changes to one of constant frequency bubble formation. Hayes et al. (2) investigated the formation of gas bubbles at submerged orifices and obtained an equation for the critical velocity separating bubble formation mechanisms which is identical to Equation (12). The fact that the present analysis predicts the onset of the constant frequency bubble formation region suggests that this region is analogous to the region in which jets form in liquid-liquid and liquid-gas systems.

The reason no visible jet forms even though the force balance predicts jet formation is because the interfacial velocity is so low that disturbances on the jet surface amplify to the magnitude of the nozzle radius a short distance from the nozzle exit. Therefore the appearance is still that of drop formation, although the drop size is now controlled by the growth rate of the fastest growing disturbance. If the disturbance growth rate is independent of nozzle velocity, the time of drop formation will be independent of velocity and the drops will be formed at a constant frequency rather than at the constant volume which results from a balance of the interfacial tension and buoyancy forces.

It is evident from the previous discussion that jet formation is generally controlled by the first mechanism postulated, the existence of a net upward force at the nozzle exit. Not only does the analysis based on this mechanism predict the jetting velocity for the wide range of liquid-liquid systems studied in the present work, but it is also consistent with results obtained in liquid-gas and gas-liquid systems. Nevertheless, the results obtained by Kintner (4) for benzyl alcohol injection into water through a 1/8-in. diameter nozzle show that merging of drops at the nozzle exit can occur prior to the more usual mode of jet formation. Equation (18) predicts a jetting velocity of 10.4 cm./sec. for this system, while Equation (10) predicts 11.0 cm./sec. The theoretical analysis is thus consistent with Kintner's results, predicting that drop merging will occur first.

The combination of the low density difference of 0.05 g./cc. and the low interfacial tension of 4.75 dynes/cm. in the benzyl alcohol-water system is responsible for the merging process. Low values of each of these parameters were studied independently in the present work, but the combination was not investigated. It is suggested that although the probability of drop merging occurring first in any system is small, its possibility should be considered by comparing the jetting velocity calculated from Equation (10) or (12) with that predicted by Equation (18).

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NOTATION

D_F = diameter of detached drop, cm.
 D_N = nozzle diameter, cm.

F_K = kinetic force, dynes
 F_P = excess pressure force, dynes
 F_S = interfacial tension force, dynes
 g = acceleration of gravity, 980 cm./sec.²
 K = numerical coefficient
 l_s = system length parameter, as defined by Equation (4)
 N_{We} = Weber number
 p, p' = pressure in continuous and dispersed phases, respectively, dynes/sq.cm.
 Q = volume flow rate of dispersed phase, cc./sec.
 U_J = jetting velocity, cm./sec.
 U_N = dispersed phase average velocity through the nozzle, cm./sec.
 U_{ri} = average rise velocity of drop over first drop diameter of rise, cm./sec.
 $U_{R\infty}$ = steady state rise velocity of drop, cm./sec.
 V_F = drop volume, cc.
 μ = continuous phase viscosity, g./ (cm.) (sec.)
 ρ, ρ' = densities of continuous and dispersed phases, respectively, g./cc.

σ = interfacial tension, dyne/cm.

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Kinetics of Physical Adsorption of Propane from Helium on Fixed Beds of Activated Alumina

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The kinetics of physical adsorption of propane from helium on fixed beds of activated alumina at 30°C. and at atmospheric pressure was studied. Two grades of activated alumina with the same average pore size distribution but different pore size distributions were used. Gas concentration, flow rate, and adsorbent particle size were also varied. The rate of internal diffusion controlled the adsorption process and was best described by Ficks' equation for unsteady state diffusion into a sphere. The internal diffusion appeared to be by a pore diffusion rather than by a surface diffusion mechanism.

The purpose of this research was to investigate the kinetics of an adsorption system in which one component was adsorbed from an inert carrier gas in a fixed-bed system. Once accurate adsorption rate data were obtained, an attempt was made to correlate these data with rate models that have been proposed in the literature. The system used here consists of propane as the adsorbate, helium as the inert carrier gas, and activated alumina as the adsorbent.

THEORY

During the adsorption of a component from a fluid passing through a bed of adsorption particles, the overall rate of adsorption can be a function of any of the following mechanisms: (1) external mass transfer from the bulk fluid phase through the boundary layer around the particle to the exterior surface of the particle; (2) surface reaction or the dynamics of the adsorption process at the fluid-solid

surface; (3) fluid phase pore diffusion into the interior of the particle; and (4) solid phase internal diffusion into the interior of the particle. In many cases, only one of these mechanistic steps controls the overall rate of adsorption.

If external mass transfer is the controlling mechanism, the rate of adsorption is described by (15)

$$\left(\frac{\partial q}{\partial t} \right)_z = \frac{k_g a_v RT}{\rho_B} (C - C^*) \quad (1)$$

whereas for the case where surface reaction is the controlling mechanism, it is described by (12, 13)

$$\left(\frac{\partial q}{\partial t} \right)_z = k_1 c (q_\infty - q) - k_2 q \quad (2)$$

If internal diffusion is the controlling mechanism, the transfer can be by two different mechanisms. For the case of fluid phase pore diffusion, the transfer rate is described by (15)

$$D_p \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r} \frac{\partial C_i}{\partial r} \right) = \epsilon \frac{\partial C_i}{\partial t} + \rho_B \frac{\partial q_i}{\partial t} \quad (3)$$

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