Combine Dimensional Analysis with Educated Guessing

Supplementary Material

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CONTENTS

I. PRESSURE DROP IN A PIPE (HAGEN-POISEUILLE LAW)

A fluid with density ρ [kg.m^{-3}] and viscosity μ [kg.m^{-1}.s^{-1}] flows at a volume rate Q [m^3.s^{-1}] through a pipe with length L [m] and radius R [m]. What is the pressure drop ΔP [kg.m^{-1}.s^{-2}] along the pipe? Perform first a dimensional analysis without any educated guess, and then simplify it to the case of laminar flow.

Hint for guessing The pressure drop ΔP is expected to be proportional to the length L of the pipe. Moreover, the density ρ should not play any role in the laminar regime.

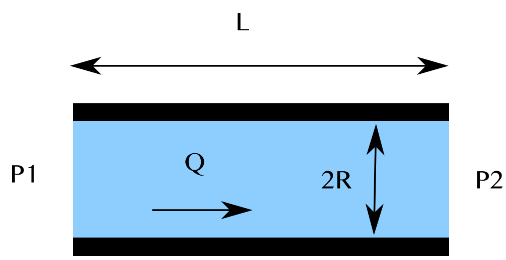

FIG. I–1. The Hagen-Poiseuille problem. A viscous liquid flows in a cylindrical pipe of length L and radius R: what is the relation between the pressure drop $\Delta P = P_1 - P_2$ and the volume flow rate Q?

Solution with no guessing. With dimensional variables the solution should take the mathematical form

$$\Delta P = F\left(Q, \rho, \mu, L, R\right) \tag{I–1}$$

That is a total of 6 variables with 3 dimensions, i.e. 3 dimensionless groups of variables. We already know at this stage that, whatever the solution is, it can can be put as

$$\Pi_0 = F\left(\Pi_1, \Pi_2\right) \tag{I–2}$$

where Π_0, Π_1 and Π_2 are 3 dimensionless groups of variables, and F is an unknown function. Equation (I–2) is already a great simplification compared to Eq. (I–1), because the number of variables to be investigated in any experiment is reduced from 5 to 2.

There is no unique way to define the dimensionless groups Π, but it does not matter because they are all equivalent in the end. A possibility consists in taking Q [m.s^{-3}], ρ

[kg.m^{-3}], and R [m] as core variables. They contain all the units (kg, m, and s) and they can therefore be used to put the remaining variables (ΔP, L, and μ) in dimensionless form. At this step, some opportunistic reasoning is always useful. For example, one may recall that ρ times velocity squared has the dimension of a pressure, which immediately suggests the following dimensionless group

$$\Pi_0 = \frac{\Delta P}{\rho (Q/R^2)^2} = \frac{R^4 \Delta P}{\rho Q^2} \tag{I–3}$$

where Q/R^2 has the dimensions of a velocity. Another dimensionless group is

$$\Pi_1 = \frac{L}{R} \tag{I–4}$$

The last group to be formed is based on the viscosity μ, which has the dimensions of pressure times seconds. One can use again the group $\rho(Q/R^2)^2$ to create the pressure units, and R^3/Q to form the seconds. This yields

$$\Pi_2 = \frac{\mu}{\rho (Q/R^2)^2 R^3/Q} = \frac{R\mu}{\rho Q} \tag{I–5}$$

The law governing the flow of viscous liquid in a pipe has therefore to be

$$\frac{R^4 \Delta P}{\rho Q^2} = F\left(\frac{L}{R}, \frac{R\mu}{\rho Q}\right) \tag{I–6}$$

Solution with guessing. The two educated guesses here are (i) that the pressure drop ΔP should be proportional to the pipe length L and (ii) that density should not play a role in the laminar regime. There are two ways to exploit these guesses. The first approach is the one we followed in the main text, which consists in starting the analysis leading to Eq. (I–6) all over again, only with variable Δ/L and without ρ. This leads to

$$\frac{\Delta P}{L} = F\left(Q, \mu, R\right) \tag{I–7}$$

There are 4 variables left and still 3 dimensions, so we are in the lucky situation where there is a single dimensionless group of variables that cannot but be a constant.

$$\Pi_0 = \text{constant} \tag{I–8}$$

To find the expression of Π_0 one can recall that the viscous stress, which is dimensionally equivalent to $\mu U/R$ where U is a velocity, has the dimension of a pressure. Using Q/R^2 as a group with the dimension of a velocity, this leads to

$$\Pi_0 = \frac{\Delta P/L}{\mu Q/R^4} \tag{I–9}$$

Expressing that Π_0 is a constant leads to

$$\boxed{\frac{\Delta P}{L} = \text{constant} \times \frac{\mu Q}{R^4}} \tag{I–10}$$

which is the well-known form of the Hagen-Poiseuille law, with the distinctive R^4 dependence.

Another way to exploit the educated guessing is starting from Eq. (I–6). Because ΔP has to be proportional to L, the unknown function $F(\Pi_1, \Pi_2)$ has to be linear in Π_1, which leads to

$$\frac{R^4 \Delta P}{\rho Q^2} = \frac{L}{R} \times F_1\left(\frac{R\mu}{\rho Q}\right) \tag{I–11}$$

where $F_1()$ is another unknown function. Moreover, because the density should not play any role, the variable ρ has to disappear from Eq. (I–11). The only possibility is that the function $F_1()$ be linear too, namely $F_1(\Pi_2) = \text{constant} \times \Pi_2$. This leads again to the Hagen-Poiseuille law as in Eq.(I–10).

II. PRESSURE DROP IN A PACKING (KOZENY-CARMAN LAW)

Same question as in the Hagen-Poiseuille problem, only with the pipe filled with a packing of small grains with diameter d [m]. How does the pressure drop depend on the grain size?

Hint for guessing If the grains are much smaller than the pipe, the flow should be homogeneous over the section. In other words, the relevant variable is not Q but $Q/(\pi R^2)$.

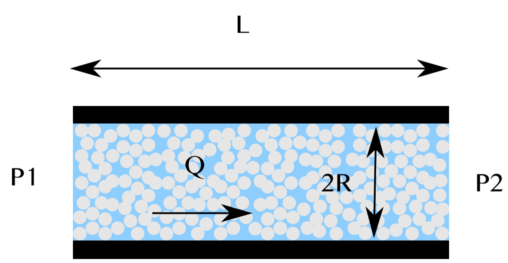

FIG. II–1. Permeability of a packed bed: the situation is identical to Fig. I–1 only with the pipe filled with small grains, in the interstices of which the fluid can flow. How is the flow rate related to the pressure drop?

Solution with no guessing With dimensional variables the solution should take the mathematical form

$$\Delta P = F\left(Q, \rho, \mu, L, R, d\right) \tag{II–1}$$

That is a total of 7 variables with 3 dimensions, i.e. 4 dimensionless groups of variables. Whatever the solution is, it can can be put as

$$\Pi_0 = F\left(\Pi_1, \Pi_2, \Pi_3\right) \tag{II–2}$$

where Π_0, Π_1, Π_2 and Π_3 are 4 dimensionless groups of variables, and F is an unknown function.

The first three dimensionless groups are identical to those identified in the Hagen-Poiseuille problem, Eqs (I–3), (I–4) and (I–5), and the extra group is here

$$\Pi_3 = \frac{d}{R} \tag{II–3}$$

The general solution has to take the form

$$\frac{R^4 \Delta P}{\rho Q^2} = F\left(\frac{L}{R}, \frac{R\mu}{\rho Q}, \frac{d}{R}\right) \tag{II–4}$$

which is a generalisation of Eq. (I–6).

Solution with guessing For the same reasons as in the Hagen-Poiseuille case, the unknown function F in Eq. (II–4) has to be linear in its first two arguments, namely

$$\frac{R^4 \Delta P}{\rho Q^2} = \frac{L}{R} \times \frac{R\mu}{\rho Q} \times F_1\left(\frac{d}{R}\right) \tag{II–5}$$

where $F1$ is an unknown function of a single variable. Rewriting Eq. (II–5), it can be put as

$$\frac{\Delta P}{L} = \frac{\mu Q}{R^4} \times F_1\left(\frac{d}{R}\right) \tag{II–6}$$

If the grains are small enough, the flow of liquid should be homogeneous over the section of the pipe. This means that if both the flow Q and the section R^2 are doubled, the pressure drop should remain the same. The relevant variable that should appear in Eq. (II–6) is therefore Q/R^2. This is only possible is F_1 has the following dependence on its argument

$$F_1\left(\Pi_3\right) = \text{constant}/\Pi_3^2 \tag{II–7}$$

The result is finally

$$\boxed{\frac{\Delta P}{L} = \text{constant} \times \frac{\mu Q/R^2}{d^2}} \tag{II–8}$$

which is nothing but Darcy's law. One therefore recovers the result that the pressure drop in a packing scales like the inverse square of the grain size.

Equation (II–6) can also be obtained by discarding/grouping dimensional variables from the beginning. Discarding the density ρ from the very beginning, and introducing the variables $\Delta P/L$ and Q/R^2, the dimensional analysis would start from

$$\frac{\Delta P}{L} = F\left(\frac{Q}{R^2}, \mu, d\right) \tag{II–9}$$

There are four dimensional variables and three dimensions, which leads to a single dimensionless number

$$\Pi_0 = \frac{(\Delta P/L)d^2}{\mu(Q/R^2)} \tag{II–10}$$

Expressing that Π_0 is a constant leads to Eq. (II–8) again.

It is interesting to note that Eq. (II–6) contains both the Hagen-Poiseuille law (Eq. I–10) and Darcy's law (Eq. II–8) as particular cases. Whether one or the other law is obtained depends on the particular form of the function $F_1()$, which can be guessed.

III. SEDIMENTATION OF PARTICLES (STOKES' LAW)

A small spherical object with radius R [m] and density ρ [kg.m^{-3}] sinks slowly in a lighter and viscous fluid with density ρ' [kg.m^{-3}] and viscosity μ[kg.m^{-1}.s^{-1}]. What is the settling velocity U [m.s^{-1}]?

Hint for guessing The variables ρ, ρ' and g can only appear under the form $(\rho - \rho') \times g$. Moreover, the settling speed should be proportional to gravity.

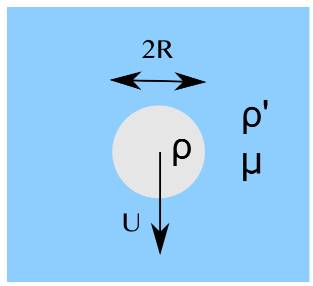

FIG. III–1. A spherical object with radius R sinks slowly in a viscous fluid. What is the sedimentation velocity?

Solution with no guessing In a brutal approach (without any educated guess) one would write the following dimensional relation

$$U = F\left(R, \rho, \rho', g, \mu\right) \tag{III–1}$$

which contains 6 dimensional variables and 3 dimensions. It can therefore be expressed in terms of 3 dimensionless groups. Using R, μ and g to put the remaining variables in dimensionless form, one obtains the following dimensionless groups

$$\Pi_0 = \frac{U}{\sqrt{Rg}} \tag{III–2}$$

$$\Pi_1 = \frac{\rho R\sqrt{Rg}}{\mu} \quad \text{and} \quad \Pi_2 = \frac{\rho' R\sqrt{Rg}}{\mu} \tag{III–3}$$

The dimensionless relation is therefore

$$\frac{U}{\sqrt{Rg}} = F\left(\frac{\rho R\sqrt{Rg}}{\mu}, \frac{\rho' R\sqrt{Rg}}{\mu}\right) \tag{III–4}$$

where $F()$ is as usual an unknown function.

Solution with guessing From our educated guesses, one has to assume that $F(\Pi_1, \Pi_2) = F_1(\Pi_1 - \Pi_2)$ where $F_1()$ is an unknown function of a single argument. One is therefore left with

$$\frac{U}{\sqrt{Rg}} = F_1\left(\frac{(\rho-\rho')R\sqrt{Rg}}{\mu}\right) \tag{III–5}$$

The second guess is that the sedimentation velocity should be proportional to g, which entails that $F_1()$ be a linear function. The final result is therefore

$$\boxed{U = \text{constant} \times \frac{(\rho-\rho')R^2 g}{\mu}} \tag{III–6}$$

which is exactly Stokes' law. Solving the equations of fluid mechanics leads to the value 2/9 for the constant in Eq. (III–6). Although dimensional analysis in itself does not tell us anything about the value of the constant, this is yet another illustration that the dimensionless constants that naturally appear in this type of analysis are of order one.

Stokes' law (Eq. III–6) can also be obtained by incorporating the educated guessing at the very beginning of the dimensional analysis. In this case, instead of Eq. (III–1), one could start with

$$\frac{U}{g} = F\left(R, \rho-\rho', \mu\right) \tag{III–7}$$

Choosing U/g as a dimensional variable is a way of enforcing the proportionality of U and g in the final result. Equation (III–7) involves 4 variables and 3 dimensions. It can therefore be expressed in terms of the single dimensionless group

$$\Pi_0 = \frac{U/g}{R^2(\rho-\rho')/\mu} \tag{III–8}$$

which has to be constant. This leads again to Stokes' law.

IV. EFFUSION OF A GAS (GRAHAM'S LAW)

There is a hole with diameter d [m^2] in a reservoir containing gas at pressure P [kg.m^{-1}.s^{-2}] temperature T [K], and molecular mass m [kg]. What is the so-called effusion rate, namely the rate $\dot{N}$ [s^{-1}] at which molecules leave the reservoir?

Hint for guessing When the hole is so small that molecules leave the reservoir one at a time, the effusion rate should be proportional to the area of the hole.

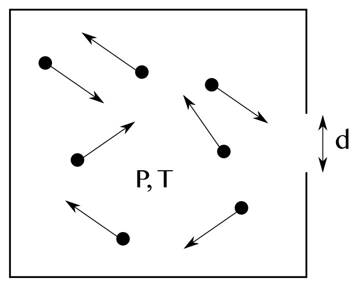

FIG. IV–1. A small hole with diameter d is made in a reservoir containing a gas at pressure P and temperature T: what is the rate at which molecules leave the reservoir through the hole?

Solution with no guessing We shall start the analysis with

$$\dot{N} = f(T, P, m, d, k_B) \tag{IV–1}$$

where we have added the Boltzmann constant k_B [kg.m^2.s^{-2}.K^{-1}] to the variables. Any universal physical constants (Planck's constant, the speed of light, etc.) can in principle intervene in any dimensional relation. There is, however, no reason to include Planck's constant if quantum effects are not expected to play a role, or the speed of light in a non-relativistic context, etc. Here Boltzmann's constant should naturally be present because effusion is a manifestation of molecular-scale thermal agitation. Moreover, in absence of k_B in the list variables it would be impossible to create a dimensionless group that would contain the temperature. Had we not included k_B, we would have reached the wrong conclusion that effusion is independent of the temperature. In light of that, T and k_B can only appear as the thermal energy k_BT [kg.m^2.s^{-2}], and we shall therefore start the analysis with the following dimensional relation

$$\dot{N} = f(k_B T, P, m, d) \tag{IV–2}$$

There are 5 variables and 3 dimensions, so 2 dimensionless numbers can be formed. There is only one combination of $k_B T$, m and d that has the same dimension as $\dot{N}$, namely $\sqrt{(k_B T/m)}/d$. The first dimensionless group is therefore

$$\Pi_0 = \frac{\dot{N} d}{\sqrt{k_B T/m}} \tag{IV–3}$$

The second and last dimensionless group has to depend on pressure. Noting that P has the dimension of an energy per unit volume, the second dimensionless group is found to be

$$\Pi_1 = \frac{P d^3}{k_B T} \tag{IV–4}$$

The relation is therefore

$$\frac{\dot{N} d}{\sqrt{k_B T/m}} = F\left(\frac{P d^3}{k_B T}\right) \tag{IV–5}$$

As such, this result already contains Graham's law, which states the rate of effusion is inversely proportional to the square root of the molecular mass.

Solution with guessing The explicit dependence on the pressure and temperature can be obtained by exploiting the educated guess that $\dot{N}$ should be proportional to the area of the hole d^2. As usual this can be done in two ways. The first way consist in starting from Eq. (IV–5), and observing that the proportionality of $\dot{N}$ to d^2 is possible only if the function $F()$ is linear. This immediately leads to

$$\boxed{\dot{N} = \text{constant} \times \frac{P d^2}{\sqrt{m k_B T}}} \tag{IV–6}$$

The other possibility consists in starting the analysis with $\dot{N}/d^2$ as a basic variable. In that case, one has 4 variables and 3 dimensions, i.e. only one dimensionless number, namely

$$\Pi_0 = \frac{\dot{N}\sqrt{m k_B T}}{P d^2} \tag{IV–7}$$

Expressing that this number is equal to a constant, one finds Graham's law (Eq. IV–6) again. A detailed calculation based on kinetic theory of gases yields the value $1/\sqrt{2\pi} \simeq 0.4$ for the unspecified constant.

V. BINARY DIFFUSION IN GASES (CHAPMAN-ENSKOG'S FORMULA)

How does the binary diffusion coefficient D_{AB} [$\mathrm{m}^2.\mathrm{s}^{-1}$] of two gases A and B depend on the temperature T [K] and pressure P [$\mathrm{kg.m}^{-1}.\mathrm{s}^{-2}$], as well as on the diameters d_A and d_B [m] and masses m_A and m_B [kg] of the molecules?

Hint for guessing The microscopic events responsible for the diffusion are two-body collisions between molecules A and B. The relevant mass in this context is the reduced mass $1/m = 1/m_A + 1/m_B$, and the molecular size plays a role via the collision cross-section $\sigma^2 = (d_A/2 + d_B/2)^2$. One may also assume that the diffusion coefficient is inversely proportional to the collision cross-section.

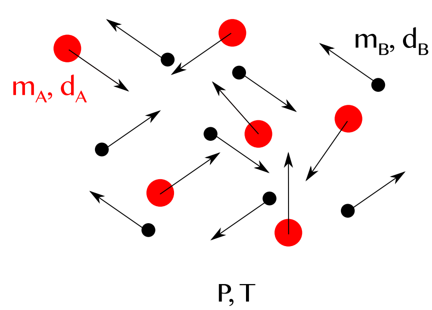

FIG. V–1. Two gases, with mass m_A and m_B, and molecular diameter d_A and d_B, collide and diffuse into one another as a consequence of their thermal motion. How does the binary diffusion coefficient depend on the pressure and temperature ?

Solution with no guessing We shall start the analysis with

$$D_{AB} = f(k_B T, P, m_A, m_B, d_A, d_B) \tag{V–1}$$

where the temperature appears as $k_B T$ for the same reason as in Eq. (IV–2). There is a total of 7 variables and 3 dimensions, which corresponds to 4 dimensionless numbers. Two numbers are easy to find, namely

$$\Pi_1 = \frac{m_A}{m_B} \quad \text{and} \quad \Pi_2 = \frac{d_A}{d_B} \tag{V–2}$$

For the others, we first look for a combination of k_BT, d_A and m_A that has the same dimensions as D_{AB}. The only solution is $\sqrt{k_BTd_A^2/m_A}$. This leads to the third number

$$\Pi_0 = \frac{D_{AB}}{\sqrt{k_BTd_A^2/m_A}} \tag{V–3}$$

One can create a last dimensionless number based on the pressure (which does not appear in Π_0, Π_1 and Π_2). That number is easily formed by noting that the pressure has the same dimensions as an energy per unit volume, which lead to

$$\Pi_3 = \frac{Pd_A^3}{k_BT} \tag{V–4}$$

The final result takes the form

$$\frac{D_{AB}}{\sqrt{k_BTd_A^2/m_A}} = F\left(\frac{m_A}{m_B}, \frac{d_A}{d_B}, \frac{Pd_A^3}{k_BT}\right) \tag{V–5}$$

This result is a bit obscure, but it already shows that diffusion scales as $m^{-1/2}$, similarly to effusion.

Solution with guessing In order to find the temperature and pressure dependence, it is easier in this context to start the analysis over with the reduced mass

$$\frac{1}{m} = \frac{1}{m_A} + \frac{1}{m_B} \tag{V–6}$$

and with the collision cross-section σ^2 [m^2] as variables instead of m_A, m_B, d_A and d_B. The relation is now

$$D_{AB} = f(k_BT, P, m, \sigma^2) \tag{V–7}$$

Because there are 5 variables and 3 dimensions, only two dimensionless numbers can be formed. By analogy with Eqs. (V–3) and (V–4), a natural choice is

$$\Pi_0 = \frac{D_{AB}}{\sqrt{k_BT\sigma^2/m}} \quad \text{and} \quad \Pi_1 = \frac{P\sigma^3}{k_BT} \tag{V–8}$$

yielding

$$\frac{D_{AB}}{\sqrt{k_BT\sigma^2/m}} = F\left(\frac{P\sigma^3}{k_BT}\right) \tag{V–9}$$

If one assumes that the diffusion coefficient ought to be inversely proportional to the collision cross-section σ^2, the unknown function has to be of the type $F(x) = \text{constant}/x$, which leads to

$$\boxed{D_{AB} = \text{constant} \times \frac{(k_BT)^{3/2}}{P\sigma^2\sqrt{m}}} \tag{V–10}$$

This is equivalent to the Chapman-Enskog expression of the binary diffusion coefficient. The unknown dimensionless multiplicative constant is indeed of order one and it can be calculated based on the so-called collision integral.

VI. EMULSIFICATION IN A TURBULENT FLOW

In an emulsification process two immiscible liquids, say water and oil (densities ρ_w and ρ_o [kg.m^{-3}], dynamic viscosities μ_w and μ_o [kg.m^{-1}.s^{-1}], and interfacial tension σ [kg.s^{-2}]), with total volumes V_w and V_o [m^3] are mixed together in a container. The mixing is done with a propeller of size D [m] that rotates at angular frequency Ω [s^{-1}]. How does the maximum size of the droplets d of the minority phase scale with Ω in the limit where the mixing is so intense as to make the flow turbulent? (This example is inspired from *Langmuir* **28** (2012) pp 104-110.)

Hint for guessing Turbulence is reached for large values of the Reynolds number. The relevant small-scale characteristic of a turbulent flow is the rate of energy dissipation per unit mass of the fluid ϵ [m^{2}s^{-3}], quite independently of how that energy is provided to the flow at large-scale.

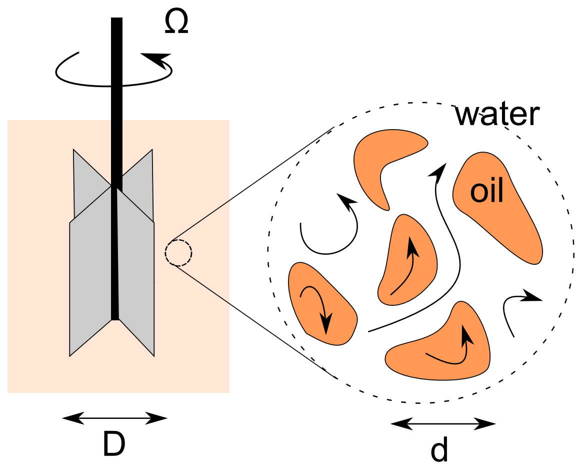

FIG. VI–1. Water and oil are mixed together in a vessel with a propeller of size D rotating at angular velocity Ω. How does the size d of the droplets that make up the emulsion depend on the operating parameters?

Solution with no guessing Writing explicitly the dependence of d on all the variables mentioned here above, one has

$$d = f\left(V_o, V_w, \rho_w, \rho_o, \mu_w, \mu_o, \sigma, D, \Omega\right) \tag{VI–1}$$

This sums up to 10 variables with 3 dimensions, yielding a total of 7 dimensionless numbers. We define the first number as the dimensionless droplet size

$$\Pi_0 = \frac{d}{D} \tag{VI–2}$$

It is also natural to define the following two numbers as the ratio of the physical properties of the two liquids

$$\Pi_1 = \frac{\mu_w}{\mu_o} \quad \text{and} \quad \Pi_2 = \frac{\rho_w}{\rho_o} \tag{VI–3}$$

as well as the following number

$$\Pi_3 = \frac{V_o}{V_o + V_w} \tag{VI–4}$$

characterising the volume fraction of oil. We may define the fifth number as the dimensionless size (or volume) of the propeller

$$\Pi_4 = \frac{D^3}{V_o + V_w} \tag{VI–5}$$

As for the remaining two numbers, the Reynolds and Weber numbers are classical in this context. The Reynolds number Re is the ratio of inertial forces to viscous forces. Using the oil phase as a reference, the Reynolds could here be defined as

$$\Pi_5 = \frac{\rho_o \Omega D^2}{\mu_o} \tag{VI–6}$$

Similarly, the Weber number We is the ratio of the inertial forces to the capillary forces. One may define it as

$$\Pi_6 = \frac{\rho_o \Omega^2 D^3}{\sigma} \tag{VI–7}$$

With these dimensionless numbers, the relation becomes

$$\frac{d}{D} = F\left(\frac{\mu_w}{\mu_o}, \frac{\rho_w}{\rho_o}, \frac{V_o}{V_o + V_w}, \frac{D^3}{V_o + V_w}, \frac{\rho_o \Omega D^2}{\mu_o}, \frac{\rho_o \Omega^2 D^3}{\sigma}\right). \tag{VI–8}$$

This equation is still uninformative, and the exact determination of F by experimental means would be prohibitive. So once again, some guess is required to proceed further.

Solution with guessing In the limit of large values of the Reynolds number, typically in turbulent conditions, the function F should no longer depend on Re. We can then write

$$\frac{d}{D} = F_1\left(\frac{\mu_w}{\mu_o}, \frac{\rho_w}{\rho_o}, \frac{V_o}{V_o + V_w}, \frac{D^3}{V_o + V_w}, \frac{\rho_o \Omega^2 D^3}{\sigma}\right). \tag{VI–9}$$

Moreover, the rate of energy dissipation per unit mass scales like $\epsilon = D^2\Omega^3$. Using that expression, one can rewrite the Weber number in Eq. (VI–9) as

$$\frac{d}{D} = F_1\left(\frac{\mu_w}{\mu_o}, \frac{\rho_w}{\rho_o}, \frac{V_o}{V_o+V_w}, \frac{D^3}{V_o+V_w}, \frac{\rho_o\epsilon^{2/3}D^{5/3}}{\sigma}\right). \quad \text{(VI–10)}$$

For a given value of ϵ, the properties of the turbulent flow at the scale at which the droplets form and coalesce are independent on the manner in which the energy is provided to the flow. In particular, they are independent of the size of the propeller. This means that F_1 cannot depend on $D^3/(V_o+V_w)$ and the dependence on the Weber number has to be of the following type

$$\frac{d}{D} = F_2\left(\frac{\mu_w}{\mu_o}, \frac{\rho_w}{\rho_o}, \frac{V_o}{V_o+V_w}\right) \times \left(\frac{\rho_o\epsilon^{2/3}D^{5/3}}{\sigma}\right)^{-3/5} \quad \text{(VI–11)}$$

where the exponent $-3/5$ is imposed by the fact that D has to cancel out in the left-hand and right-hand sides. Note that the function F_2 depends only on the quantities and properties of the two immiscible liquids. As far as the propeller operation is concerned, F_2 can therefore be considered constant, yielding

$$\boxed{\frac{d}{D} = \text{constant} \times \left(\frac{\rho_o\Omega^2D^3}{\sigma}\right)^{-3/5}.} \quad \text{(VI–12)}$$

A single experiment would be sufficient to determine the pre-factor of this scaling law.

We can then discuss the limit of validity of Eq. (VI–12), which depends on our assumption of negligible viscous effects. As turbulence is multi-scale by nature, the relative importance of inertial and viscous effects depends on the particular scale considered. At the scale of the propeller, viscosity is negligible. However, this need not be the case at the scale of the droplet. At the scale d of droplets, the relative importance of inertia and viscosity can be quantified through an appropriate Reynolds number R_d. By construction, this number has to be proportional to ρ_o/μ_o. It should also depend on the scale d. As the flow is turbulent, its only relevant characteristic is the energy dissipation rate per unit mass ϵ. The only dimensionless variable that can be formed according to these constraints is

$$Re_d = \frac{\rho_o\epsilon^{1/3}d^{4/3}}{\mu_o} \quad \text{(VI–13)}$$

Viscosity is then of negligible influence on the emulsification when $Re_d > 1$, which gives when combined with Eq.(VI–12):

$$\epsilon = D^2\Omega^3 < \frac{\rho_o\sigma^4}{\mu_o^5}F_2^{20/3} \quad \text{(VI–14)}$$

This yields a maximum operating rotation speed Ω, above which Eq.(VI–12) is no longer valid.

VII. EFFECTIVENESS FACTOR OF A CATALYTIC PELLET (THIELE MODULUS)

Many chemical reactions take place in porous solid catalysts into which the reactant molecules have to diffuse before they can reach the active sites and react. Imagine a spherical catalyst pellet with radius R [m] and kinetic constant k_V [s^{-1}] per unit volume, in contact with a reactant in concentration c [$mol.m^{-3}$]. The diffusion coefficient of the reactant in the pellet is D [$m^2.s^{-1}$]. What is the reaction rate $\dot{N}$ [$mol.s^{-1}$] in the case where diffusion is limiting the rate?

Hint for guessing When the reaction is diffusion-limited, it necessarily takes place close to the surface of the pellet so that $\dot{N}$ is proportional to the area of the pellet.

Solution with no guessing The relation we look for is of the type

$$\dot{N} = f\left(c, k_V, R, D\right) \tag{VII–1}$$

There are 5 variables based on 3 units ([mol], [m] and [s]), and the problem can therefore be expressed in terms of only 2 dimensionless numbers. The first number can be obtained by noting that the simplest combination of variables with the same dimension as $\dot{N}$ is $R^3 k_V c$, which leads to

$$\Pi_0 = \frac{\dot{N}}{R^3 k_V c} \tag{VII–2}$$

The second dimensionless number has to include the diffusion coefficient D [$m^2.s^{-1}$] in its definition. It can be put in dimensionless form in the following way

$$\Pi_1 = \frac{D}{R^2 k_V} \tag{VII–3}$$

The solution of the reaction-diffusion problem can therefore be put as

$$\frac{\dot{N}}{R^3 k_V c} = F\left(\frac{D}{R^2 k_V}\right) \tag{VII–4}$$

Solution with guessing In the diffusion-limited regime, the reactant molecules do not have enough time to diffuse to the center of the pellet before they react. Because the reaction only occurs close to the surface, $\dot{N}$ has to be proportional to the outer area of the pellet,

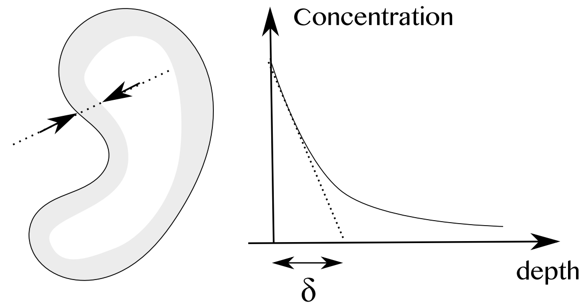

FIG. VII–1. Qualitative concentration distribution in a catalytic pellet of arbitrary shape (left) for large reaction rates: the concentration decreases in a thin region close to the surface. The thickness δ of that region can be defined precisely by extrapolating the profile as shown on the right.

i.e. to R^2. This means that the analytical form of the function $F()$ in Eq. (VII–4) has to be $F(\Pi_1) = \text{constant} \times \sqrt{\Pi_1}$. The final result is therefore

$$\frac{\dot{N}}{R^3 k_V c} = \text{constant} \times \sqrt{\frac{D}{R^2 k_V}} \tag{VII–5}$$

This result is usually expressed slightly differently, in terms of the effectiveness factor

$$\eta = \frac{\dot{N}}{4/3\pi R^3 k_V c} = \frac{3}{4\pi}\Pi_0 \tag{VII–6}$$

which is the ratio of $\dot{N}$ and the reaction rate that would be obtained in the case where diffusion would be much faster than reaction. In that case the concentration would be homogeneous over entire catalyst pellet and equal to the external value c, so that $\dot{N} = 4/3\pi R^3 k_V c$. Moreover, one also defines the Thiele modulus ϕ as

$$\phi = \sqrt{\frac{k_V R^2}{D}} = 1/\sqrt{\Pi_1} \tag{VII–7}$$

In terms of these new dimensionless numbers, Eq. (VII–5) can be written as

$$\boxed{\eta = \frac{\text{constant}}{\phi}} \tag{VII–8}$$

which is a classical result of chemical engineering. The full solution of the problem, obtained by solving the reaction/diffusion equation is spherical coordinates yields the exact value constant $= 3$, which is of order of unity as expected.

The analysis here above concerned a spherical pellet, but it can be generalised to pellets of any shape as sketched in Fig. VII–1. In the case where the reaction is faster than the time needed for a molecule to diffuse over a distance comparable to the size of the pellet, the concentration profile is expected to be as in Fig. VII–1. There is a thin layer of thickness δ where the concentration is finite and further away from the surface the concentration is practically zero. If necessary, δ can be defined rigorously as the intercept of the concentration profile as shown in Fig. VII–1.The general dependence of δ is the following

$$\delta = f(D, c, k_V, L) \tag{VII–9}$$

where L is a characteristic size of the pellet. In the case of a pellet with arbitrary shape, L can be estimated as V/A where V and A are the pellet volume and outer area, respectively. In the limit of fast reaction, however, the layer is so thin that we do not expect the shape or size of the pellet to matter at all. In this limit the dependence becomes much simpler

$$\delta = f(D, c, k_V) \tag{VII–10}$$

Because L is no longer among the variables, there are only 4 variables and 3 dimensions left. There is therefore a single dimensionless number, which is conveniently written as $\Pi_0 = \delta/\sqrt{D/k_V}$. Buckingham's theorem therefore leads to

$$\delta = \text{constant} \times \sqrt{\frac{D}{k_V}} \tag{VII–11}$$

where the unknown constant is, as usual, expected to be of the order of unity.

Because we have defined δ in terms of the concentration gradient, the total number of molecules that diffuse into the catalyst pellet can be written as

$$\dot{N} = AD\frac{c}{\delta} \tag{VII–12}$$

were A is the outer area of the pellet, without any unknown dimensionless constant. Because we have assumed that the catalyst is working in stationary conditions, the number of molecules that diffuse into the pellet is equal to the number of molecules that react inside the pellet. So $\dot{N}$ has the same meaning as before. On the other hand, the effectiveness factor for a pellet of arbitrary shape is defined as a function of the volume as follows

$$\eta = \frac{\dot{N}}{V k_V c} \tag{VII–13}$$

Putting Eqs. (VII–11) and (VII–13) together yields the result

$$\eta = \frac{1}{\text{constant}}\,\frac{1}{\phi'} \tag{VII–14}$$

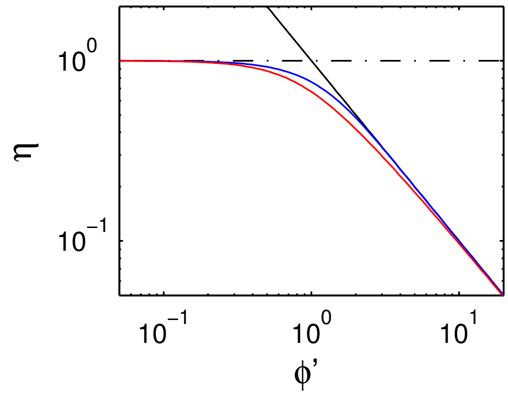

FIG. VII–2. Effectiveness factor η as a function of ϕ': the solid black line is Eq. (VII–14) and the horizontal dashed line is $\eta = 1$, both obtained from dimensional analysis and guessing. The two coloured lines are the expressions obtained by solving the complete diffusion-reaction equation for a plate-like (blue) and spherical (red) catalyst pellet.

where the constant is the one introduced in Eq. VII–11, and the Thiele modulus ϕ' is now defined in terms of the size V/A

$$\phi' = \sqrt{\frac{k_V}{D}\left(\frac{V}{A}\right)^2} \tag{VII–15}$$

Naturally, Eq. (VII–14) contains Eq. (VII–8) as a particular case, for $V/A = R/3$ as is the case for a sphere. In particular, the unknown constant in Eq. (VII–14) is independent of the pellet shape. From the known value constant'$= 3$ in Eq. (VII–8), one reaches the conclusion that the constant in Eq. (VII–14) is exactly equal to one.

This more detailed dimensional analysis enables us to determine the domain of validity of Eq. (VII–14). It should be valid as long as the thickness δ is much smaller than the size of the pellet V/A. Using Eq. (VII–11) to estimate δ, this can be written as

$$\phi' \gg 1 \tag{VII–16}$$

The other limit, $\phi' \ll 1$, corresponds to the situation where $\delta \gg V/A$. In that case, the concentration is almost homogeneous throughout the pellet, which means that the effectiveness factor is equal to one, $\eta = 1$. The overall situation is summarised in Fig. VII–2, in which the asymptotic expressions obtained by dimensional analysis are compared with exact results for plate-like and spherical pellets (see *e.g.* Bird, Stewart and Lightfoot, *Transport Phenomena*, 2nd edition, Wiley, 2007).

The asymptotic behaviours of the curve are universal; they do not depend on the shape of the pellet, however complicated it may be. The shape of the pellet only influences the curve $\eta(\phi')$ in the region $\phi' \sim 1$ where both large-ϕ' and small-ϕ' asymptotes cross each other.