Supplemental material

The Concept of the Osmotic Engine

To evaluate the Gibbs free energy of mixing in a solution, this supplemental material introduces a conceptual and alternative design for the energy-generating process, operating in the pressure region of $0 < \Delta P \leq \Delta\pi$, called pressure retarded osmosis[20–25], PRO. The PRO process itself is not within the scope of this material, as it has already been extensively studied elsewhere in the literature[26–32]. Instead, this material focuses on the osmotic engine — a new conceptual design that can be used as a measuring device. The osmotic engine consists of at least three cylinders on the same engine block, with the possibility of additional cylinders. For better comprehension, the optimal configuration of the osmotic engine comprises four cylinders labeled as C_1, C_2, C_3, and C_4.

The Cylinder

In order to ensure proper functioning of the osmotic engine, it is necessary to connect the cylinder to reservoirs containing a solvent, a *Test* solution, and a osmotic diluted *Test* solution through three distinct ducts. The cylinder is made up of several components including a cylinder head, piston, piston ring, connection rod, crankshaft, cylinder, and a semipermeable membrane. Essentially, the osmotic engine is a conversion of an existing internal combustion engine, with the cylinder, piston ring, and piston fitting together seamlessly to prevent any leakage of solution between the piston and the semipermeable membrane via the cylinder. To withstand high pressure during the working stroke, the semipermeable membrane must be mechanically supported on the low-pressure side. Additionally, for the membrane to generate PV-work on the surroundings, it should be selected based on high values of L_p, which can be determined through measurements[19] or from literature[34]. Furthermore, the membrane should be selected for its semipermeability, allowing only the solvent to permeate and not the solute, especially when the engine is used as an osmometer.

Logical Components

The arrangement of the cylinder requires the inclusion of three valves, specifically valve one, v_1, valve two, v_2, and valve three, v_3, as shown in Fig.(4(a)) or Fig.(6(a)). Each valve can have either of two boolean values: 1 for open and 0 for closed. The valve train can assume stroke-dependent states during the filling stroke, F, working stroke, W, first part of exhaustion stroke, E_1, and second part of exhaustion stroke, E_2, as depicted in the matrix below

$$\begin{array}{l c} & \begin{array}{ccc} v_1 & v_2 & v_3 \end{array} \\ \begin{array}{l} \text{Fill stroke, } F \\ \text{Working stroke, } W \\ \text{Exhaustion stroke, } E_1 \\ \text{Exhaustion stroke, } E_2 \end{array} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 1 \end{pmatrix} \end{array}$$

The cylinder can perform PV-work on the surrounding environment only during the working stroke. During the other strokes, it needs to be propelled forward by the other cylinders, as elaborated in the subsequent section, as well as in Tab.(2(a)), Fig.(5(b)) and Fig.(6(b)). When cylinder C_3 is in its filling stroke, it is propelled forward by the working stroke of cylinder C_2 via the crankshaft. During its working stroke, it drives the other pistons on the crankshaft through their respective strokes. During its first exhaustion stroke, it is propelled by the working stroke of cylinder C_4. Finally, during its second exhaustion stroke, it is propelled by the working stroke of cylinder C_1. Together with the valves a unit on the crankshaft used to regulate the engine torque, τ_E, is considered a logical component of the engine.

Fill fraction α	Number of cylinders N	Piston position	Filled volume V_F	Displaced volume V_D
1/3	3	P_1	0	–
1/2	4	P_2	αV_C	0
3/4	8	P_3	V_C	$(1-\alpha)V_C$

Table 1 Please note that, for an engine based on the simple design, one cycle corresponds to two full working strokes, equivalent to a total displaced volume of $2V_C$. This knowledge proves useful when selecting the appropriate *Test* volume, $V(Test)$, and solvent volume, V_A, respectively, for calibrating the device to identify the critical dilution factor, see Fig.(9) and Fig.(10).

Working Principle

When the piston is placed in the top position in C_3 it is referred to be in position 1, P_1. In this position, the valves enter the state $(v_1, v_2, v_3) = (1,0,0)$. Driven by another cylinder on the crankshaft, C_2, see Tab.(2(a)), which is in its working stroke, the piston is driven toward a position where the cylinder is filled αV_C with the *Test* solution. This position is referred to as position 2, P_2. Because $v_2 = 0$ solvent cannot permeate through the semipermeable membrane and as such the osmotic process is prohibited during the fill stroke. Thus, the cylinder volume, V_C, is divided into a part to which the *Test* solution is sucked and a part to which solvent later flows due to the osmotic transport process. When the piston is in P_2, the cylinder is partially filled with the solution, with a fraction of α, where $0 < \alpha < 1$, of the cylinder volume. The filled volume, V_F, where $0 \leq V_F \leq \alpha V_C$, and the displaced volume, V_D, where $0 \leq V_D \leq (1-\alpha)V_C$ is illustrated in Tab.(1).

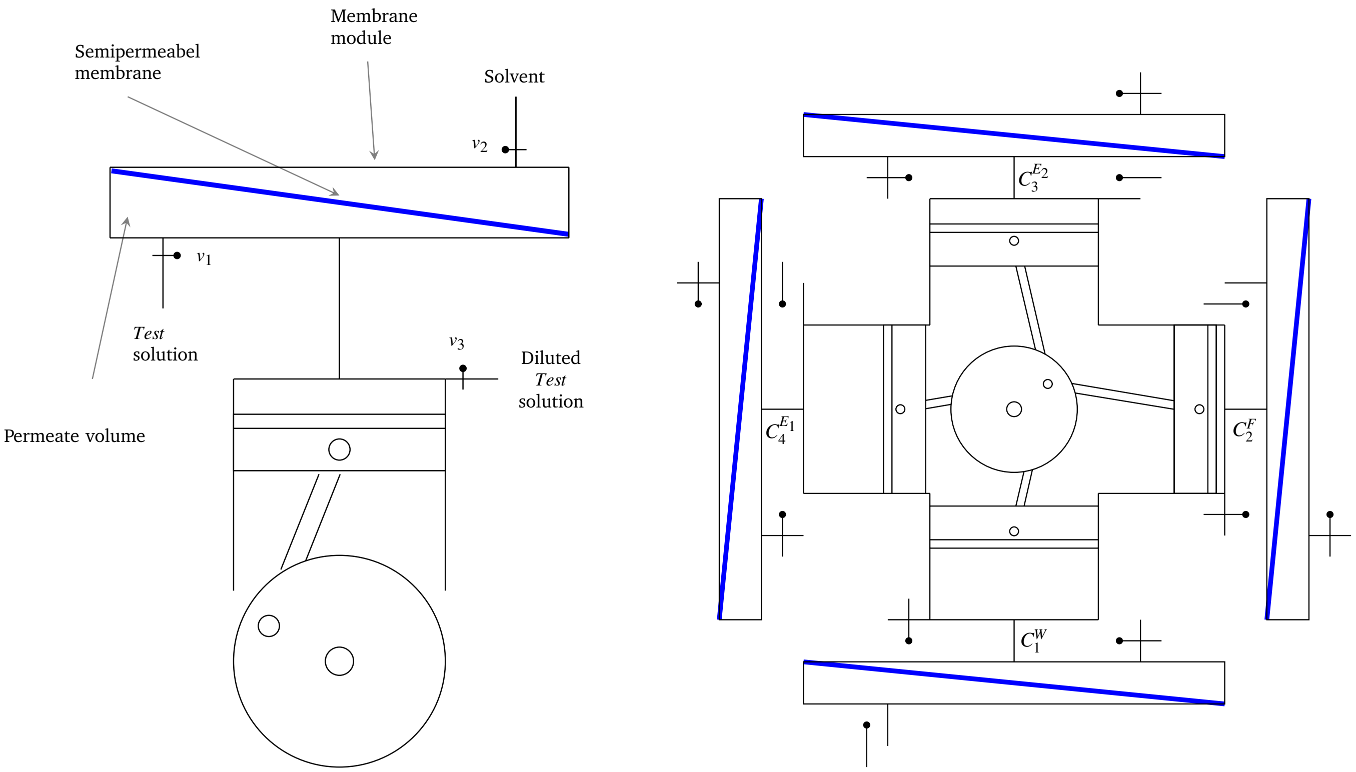
The working principles presented above are also expressed graphically in Fig.(7). In this configuration, the filling stage is carried out with $v_2 = 0$, ensuring that solvent transport across the semipermeable membrane is suppressed during the fill stroke. Subsequently, the osmotic transport is enabled by switching to the appropriate valve state, such that solvent can enter the cylinder volume that was reserved for dilution. As a consequence, the protocol remains well-defined even for highly concentrated *Test* solutions, since the mechanical separation between the filled volume V_F and the displaced volume V_D is maintained throughout the cycle.

For systems where the *Test* solution contains a solute molecule of very high molecular weight, an alternative engine layout is recommended. In Fig.(8), a divided-stroke design is shown, in which the filling and osmotic dilution stages are distributed over distinct piston motions (or sub-strokes). This separation reduces sensitivity to slow equilibration and large solution viscosities, and it improves operational robustness when membrane transport kinetics become limiting. Consequently, the divided-stroke design is preferred for macromolecular solutes, whereas the full-stroke configuration in Fig.(7) is generally sufficient for lower-molecular-weight solutes and for concentrated solutions where rapid cycling is desired.

When the cylinder is filled with the fraction of α with the solution, the piston is in P_2, where the valves enter the state: $(v_1, v_2, v_3) = (0,1,0)$. With these valve values, the solvent will spontaneously permeate through the semipermeable membrane and starts to build up a hydrostatic pressure difference between the solvent and the solution compartment. In the working stroke, a volume of V_D is displaced, and to ensure that the desired effect is produced - that is to say, that Eq.(48) is satisfactorily met - torque must be applied to the crankshaft. When C_3 is completely filled with diluted solution, it is referred to be in position 3, P_3, where the valves enter the state: $(v_1, v_2, v_3) = (0,0,1)$. The piston will now be moved back to P_1, while the diluted solution is exhausted from the cylinder. This movement is accomplished by two working strokes: Firstly from C_4, and secondly from C_1, see Tab.(2(a)).

Calibrating the Conceptual Osmotic Engine

In the following, quantities carrying the subscript C are defined at the level of an individual cylinder of the osmotic engine, with cross-sectional



(a) This setup is more realistic, when the engine's primary objective is to harness energy from the *Test* solution: Please notice that a pressure nozzle to the atmosphere in the solvent compartment, is not needed for this application.

(b) Engine with four cylinders, in the simple design where $\alpha = 1/2$.

Fig.(6) The simple design is a non-overlapping sequential design, where the pistons work in turn and their working strokes do not overlap each other on the crankshaft. (a) The permeate volume, V_P, must full-fill: $V_P \leq V_C$. (b) It can be shown that the number of membrane modules can be reduced to only two, if the number of cylinders is an even number.

Cylinder	*Strokes*			
C_1	W	E_1	E_2	F
C_2	F	W	E_1	E_2
C_3	E_2	F	W	E_1
C_4	E_1	E_2	F	W

(a) The simple design with $\alpha = 1/2$, where only one piston works at a time.

Cylinder	*Strokes*							
C_1	W_1	W_2	E_1	E_2	E_3	E_4	F_1	F_2
C_2	F_2	W_1	W_2	E_1	E_2	E_3	E_4	F_1
C_3	F_1	F_2	W_1	W_2	E_1	E_2	E_3	E_4
C_4	E_4	F_1	F_2	W_1	W_2	E_1	E_2	E_3
C_5	E_3	E_4	F_1	F_2	W_1	W_2	E_1	E_2
C_6	E_2	E_3	E_4	F_1	F_2	W_1	W_2	E_1
C_7	E_1	E_2	E_3	E_4	F_1	F_2	W_1	W_2
C_8	W_2	E_1	E_2	E_3	E_4	F_1	F_2	W_1

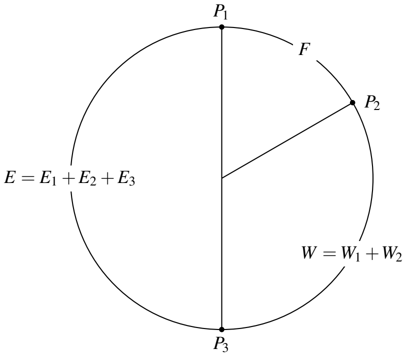
(b) A more complex configuration with $\alpha = 1/2$ enables the concurrent operation of two pistons. However, this arrangement is not recommended as the piston in the W_1-working stroke either slows down or damages the membrane associated with the piston in the W_2-working stroke.

Table 2 The application of electric load management, by connecting the crankshaft to an electric generator, enables precise control of the engine's crank angular velocity, ω_E, through adjustment of the extracted electrical current.

area A_C and volume V_C. In particular, $n_C(A)$ and $n_C(B)$ denote the amounts of A and B contained in one cylinder. The constants $\mathbf{V}^*_{\mathbf{A}}$ and $\mathbf{V}^*_{\mathbf{B}}$ denote the molar volumes of the pure components A and B, respectively, and $\mathbf{M}(\mathbf{A})$ and $\mathbf{M}(\mathbf{B})$ denote their molar masses.

Non-additive Volume *Test* Solutions

The purpose of this subsection is to establish that, when a cylinder in the osmotic engine is considered in the hypothetical case where the piston can displace the atmosphere without limitation, the volumetric expansion required to attain osmotic equilibrium is denoted by $\Delta V_C^{eq}(Test)$, and that

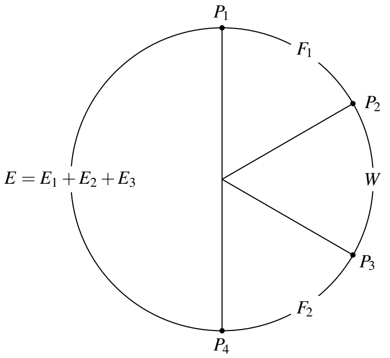


(a) Full-stroke design: The end of the working stroke, P_3, is situated in the bottom position of the crank.

Cylinder	*Strokes*					
C_1	W_1	W_2	E_1	E_2	E_3	F
C_2	E_3	F	W_1	W_2	E_1	E_2
C_3	E_1	E_2	E_3	F	W_1	W_2

(b) Composition table for a full-stroke three-cylinder osmotic engine, optimized to minimize the number of cylinders: $N = \frac{2}{1-\alpha}$, with $\alpha = 1/3$.

Fig.(7) Note that P_3 occupies the bottom position, and it is anticipated that only a significantly large value of ΔP is capable of rotating the crankshaft to this position. Therefore, a necessary condition for this occurrence is a test solution with a relatively high osmotic pressure.



(a) Divided-stroke design: The end of the working stroke, P_3, is not situated in the bottom position of the crank, at the cost of extra cylinders.

Cylinder	*Strokes*					
C_1	W	F_2	E_1	E_2	E_3	F_1
C_2	F_1	W	F_2	E_1	E_2	E_3
C_3	E_3	F_1	W	F_2	E_1	E_2
C_4	E_2	E_3	F_1	W	F_2	E_1
C_5	E_1	E_2	E_3	F_1	W	F_2
C_6	F_2	E_1	E_2	E_3	F_1	W

(b) This composition table shows that the addition of an extra intake, F_2, necessitates a doubling of the number of cylinders if α is fixed; see Fig.(7(b)).

Fig.(8) If the binary *Test* solution incorporates a solute with a significantly large molecular weight, it may become imperative to displace P_3 from the bottom position of the crankshaft. This adjustment reduces both V_C and the critical osmotic pressure. It is beyond the scope of this article to derive equations analogous to Eq. (56), Eq. (57), and Eq. (59); however, the derivation follows the same principles.

---

the corresponding relative expansion ψ can be defined by

$$\alpha V_C + \Delta V_C^{eq}(Test) = (1+\psi)\cdot \alpha V_C \tag{S1}$$

It is then shown that this same factor ψ is obtained operationally when the exhaust volume is recirculated to the external *Test* solution, such that

$$V(Test) + \Delta V^{stop}(Test) = (1+\psi)\cdot V(Test) \tag{S2}$$

i.e. the relative expansion from αV_C to $\alpha V_C + \Delta V_C^{eq}(Test)$ in the hypothetical static-osmometry picture is identical to the relative volume increase of the external *Test* solution at engine stall. Finally, Fig.(9) provides a direct practical blueprint for implementing the recirculation-based dilution procedure and for determining ψ experimentally.

A *Test* solution of volume $V(Test)$, containing an amount of substance $n(B)$ of solute B dissolved in solvent A, is considered. This solution is associated with an osmotic cylinder, as illustrated in Fig.(9). During the filling stroke F, the total amount of solute drawn into the cylinder, $n_C(B)$, is given by

$$n_C(B) = n(B)\left(\frac{\alpha V_C}{V(Test)}\right) \tag{S3}$$

After a hypothetical osmotic equilibrium has been reached, characterized by the unknown equilibrium volume $V_C^{eq}(Test)$, the solute concentration in the cylinder is expressed as

$$C_C^{eq}(B) = \frac{n_C(B)}{V_C^{eq}(Test)} \tag{S4}$$

Since $n_C(B) = n(B)\left(\frac{\alpha V_C}{V(Test)}\right)$, this can be rewritten as

$$C_C^{eq}(B) = \frac{n(B)}{V(Test)}\left(\frac{\alpha V_C}{V_C^{eq}(Test)}\right) \tag{S5}$$

When the exhaust volume is recirculated, as shown in Fig.(9), pure solvent A is continuously added to the *Test* solution while the amount of solute B remains constant. This gradual dilution of the *Test* solution leads to a decrease in both osmotic pressure and the hypothetical equilibrium volume until the condition

$$\alpha V_C < V_C^{eq}(\text{Dilute } Test) < V_C \tag{S6}$$

is fulfilled. At this point, the engine comes to a complete halt, as illustrated in Fig.(4(b)). Moreover, $V_C^{eq}(\text{Dilute } Test) \to V_C$ as $\alpha \to 1$.

The additional volume added to the external *Test* solution is referred to as the measured value $\Delta V^{stop}(Test)$, and the total diluted volume is given by

$$V(Test) + \Delta V^{stop}(Test) = (1+\psi)V(Test) \tag{S7}$$

where $\psi = \Delta V^{stop}(Test)/V(Test)$ is defined as the critical dilution factor.

The total critical amount of substance drawn into the cylinder just before halting, $n_C^{cri}(B)$, is then given by

$$n_C^{cri}(B) = n(B)\left(\frac{\alpha V_C}{(1+\psi)V(Test)}\right) \tag{S8}$$

where again $\alpha \to 1$.

This amount represents the threshold that prevents the equilibrium volume from exceeding the cylinder volume V_C. If an additional amount of solute equal to

$$\left(V_C^{eq}(Test) - V_C\right) C_C^{eq}(B) \tag{S9}$$

is added, the unknown equilibrium volume $V_C^{eq}(Test)$ is restored. It then follows that

$$n_C(B) = n_C^{cri}(B) + \left(V_C^{eq}(Test) - V_C\right) C_C^{eq}(B) \tag{S10}$$

Upon substitution of Eq.(S3), Eq.(S8) and Eq.(S5) into Eq.(S10), one obtains

$$\frac{\alpha V_C}{V(Test)} = \frac{\alpha V_C}{(1+\psi)V(Test)} + \left(V_C^{eq}(Test) - V_C\right)\frac{1}{V(Test)}\,\frac{\alpha V_C}{V_C^{eq}(Test)}$$

$$1 = \frac{1}{1+\psi} + 1 - \frac{V_C}{V_C^{eq}(Test)}$$

$$V_C^{eq}(Test) = (1+\psi)V_C \tag{S11}$$

Accordingly, the hypothetical volume change associated with osmotic expansion from the initial volume αV_C to the equilibrium volume $V_C^{eq}(Test)$ is given by

$$\Delta V_C^{eq}(Test) = V_C^{eq}(Test) - \alpha V_C = (1+\psi)V_C - \alpha V_C = (1-\alpha+\psi)V_C \tag{S12}$$

It is noted that $\Delta V_C^{eq}(Test) \to \psi V_C$ as $\alpha \to 1$, corresponding to a hypothetical osmotic engine equipped with an infinite number of cylinders.
As demonstrated above, there is an equality between the critical dilution factor ψ, which stops the osmotic engine, and the osmotic dilution factor that results in the hypothetical equilibrium volume $V_C^{eq}(Test)$. As mentioned, the osmotic pressure that causes the engine to stop is called the critical osmotic pressure, $\Delta\pi_{cri}(Test)$. At engine stall, the piston in the working cylinder must be positioned between the intake volume αV_C and the maximum volume V_C, leading to the pressure inequality $\min(P) \le \min(P) + \Delta\pi_{cri}(Test) \le \max(P)$ where

$$\min(P) = \left(\frac{\alpha V_C}{A_C}\right)\cdot \rho_{cri}(Test)\cdot \mathbf{g} \tag{S13}$$

and where

$$\begin{aligned}
\max(P) &= \left(\frac{V_C}{A_C}\right)\cdot \tilde{\rho}_{cri}\cdot \mathbf{g}\\
&= \left(\frac{V_C}{A_C}\right)\left(\frac{\alpha V_C\cdot \rho_{cri}(Test) + (1-\alpha)V_C\cdot \boldsymbol{\rho^*(A)}}{\alpha V_C + (1-\alpha)V_C}\right)\mathbf{g}\\
&= \left(\frac{V_C}{A_C}\right)\left(\alpha\rho_{cri}(Test) + (1-\alpha)\boldsymbol{\rho^*(A)}\right)\mathbf{g}\\
&= \min(P) + \left(\frac{V_C}{A_C}\right)(1-\alpha)\boldsymbol{\rho^*(A)}\,\mathbf{g}
\end{aligned} \tag{S14}$$

When inserted into the inequality, this gives

$$\min(P) \le \min(P) + \Delta\pi_{cri}(Test) \le \min(P) + \left(\frac{V_C}{A_C}\right)(1-\alpha)\cdot\boldsymbol{\rho^*(A)}\cdot\mathbf{g} \tag{S15}$$

which simplifies to

$$0 \le \Delta\pi_{cri}(Test) \le \left(\frac{V_C}{A_C}\right)(1-\alpha)\cdot\boldsymbol{\rho^*(A)}\cdot\mathbf{g} \tag{S16}$$

When Eq.(S16) is normalized with respect to the standard pressure $\mathbf{P}^\circ = \left(\frac{V_C}{A_C}\right)\cdot\boldsymbol{\rho^*(A)}\cdot\mathbf{g} = 1$ bar, the following relationship is observed

$$0 \le \Delta\pi_{cri}(Test) \le (1-\alpha)\mathbf{P}^\circ \tag{S17}$$

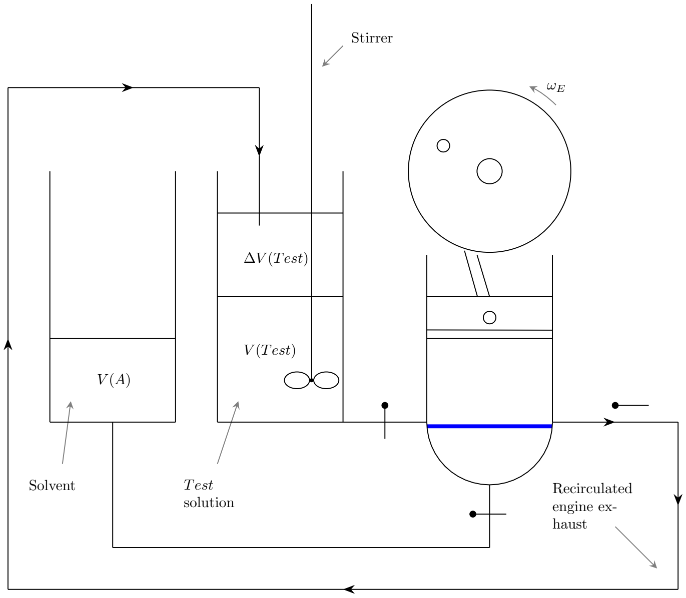


Fig.(9) Note that the pressure leveling nozzle and the manometer, as depicted in Fig.(4(b)), are not shown in this figure for the sake of simplicity. Please recall that: $\omega_E \to 0$ for $\Delta V(Test) \to \Delta V^{stop}(Test)$.

The dilution process, which aims to stop the osmotic engine, is simply carried out, as illustrated in Fig.(9). The subsequent determination of ψ can be achieved by extrapolating a regression graph to the point $(\psi, 0)$, as shown in Fig.(10). Should this method lack sufficient accuracy, a straightforward precision titration of the *Test* solution with solvent A will be adequate. It is important to note that the values of $\Delta V/V(Test)$ and ω_E are obtained through straightforward measurements. Specifically, ω_E is measured at the crankshaft, and the actual total volume of the *Test* solution is measured directly in its container.

Please notice that for fixed cylinder volume V_C, the minimum volume of the *Test* solution, $\min\{V(Test)\}$, is expressed as

$$\begin{aligned}
\min\{V(Test)\} &= N\cdot\alpha V_C\\
&= \left(\frac{2\alpha}{1-\alpha}\right)V_C
\end{aligned} \tag{S18}$$

Additive-Volume *Test* Solutions and Multi-Cylinder Osmotic Engines

As the solute B is progressively diluted by the solvent A, a localized solvation structure is expected to be established around B, which may be interpreted as an effective coordination environment. After formation of a primary solvation shell, B is increasingly screened from subsequently added solvent, in the sense that any secondary (or higher-order) solvation structure is progressively more bulk-like and contributes more weakly to non-additive mixing effects. Additional A therefore predominantly experiences solvent–solvent interactions in the bulk phase. In the dilute limit, the macroscopic volume increment upon further addition of A is therefore taken to be effectively volume-additive. The incremental volume is governed primarily by the added solvent, while any non-additive mixing effects are confined to the local solvation zone around B and become negligible as $\rho(Test) \to \boldsymbol{\rho^*(A)}$.

The above argument suggests that, for sufficiently dilute *Test* solutions, non-additive mixing effects are confined to a local solvation zone around B, and the net volume increment upon adding A may be idealized as effectively additive, i.e. $V_C(Test) \approx n_C(A)\mathbf{V}_\mathbf{A}^* + n_C(B)\mathbf{V}_\mathbf{B}^*$ in the dilute limit. This volume-additivity assumption will be adopted in the following derivation in order to relate the osmotic driving force to an equivalent hydrostatic

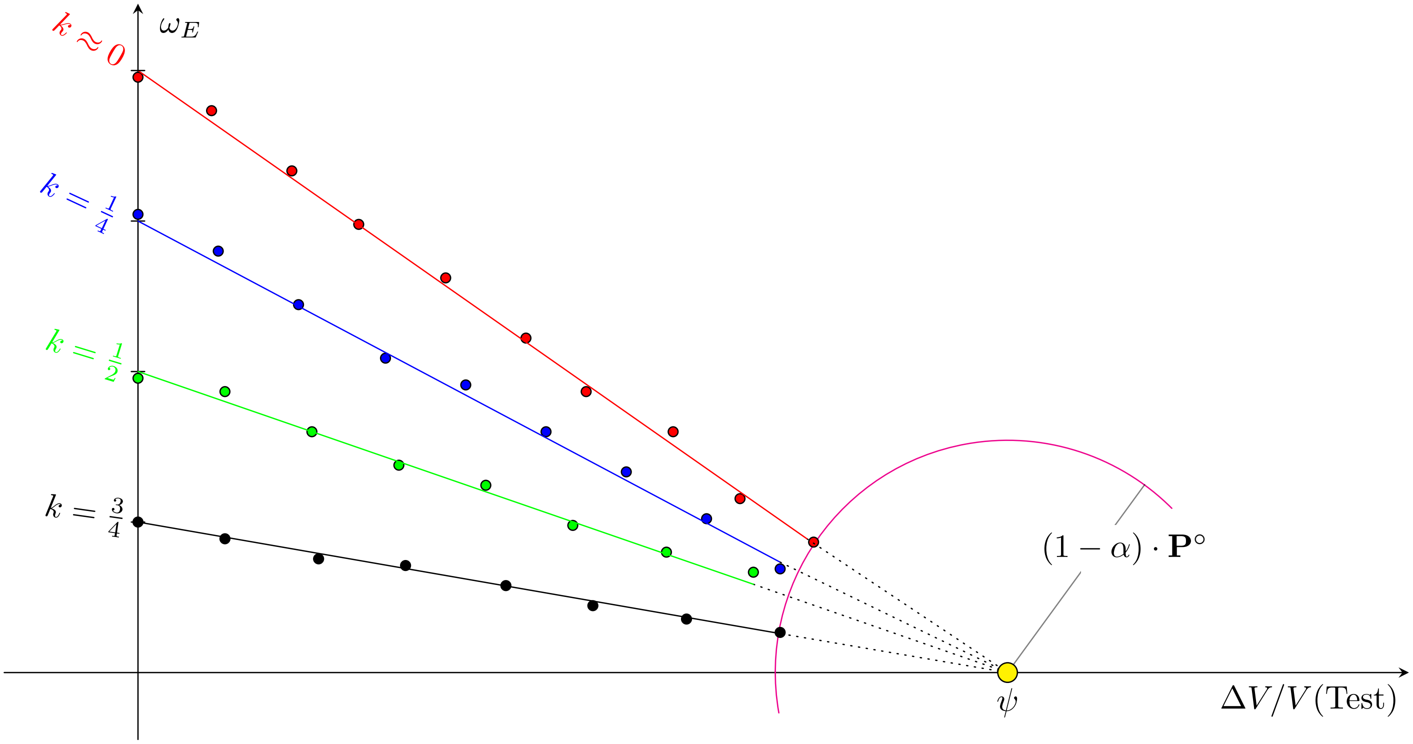


Fig.(10) The magenta circle, centered at the point $(\psi,0)$, is the final extrapolated correlation between the angular velocity of the crankshaft and the critical dilution factor at which the engine stalls. The corresponding radius, represented by $(1-\alpha)\cdot\mathbf{P}^\circ$, decreases as α approaches unity. Consequently, it is expected that an osmotic engine with eight cylinders, $\alpha = 3/4$, will provide a more accurate estimate of ψ compared to an engine with only three cylinders, $\alpha = 1/3$. The parameter k in Eq.(54) reflects the load on the crankshaft. It is important to note that $k = 0$ is purely theoretical, as there are no weightless moving components in real engines, and frictionless engines do not exist.

pressure difference.

In the dilute-limit idealization underlying volume additivity, the *Test* solution is here further treated as van't Hoff ideal. This part of the supplementary material therefore derives $n_C(B)\cdot\partial\psi/\partial n_C(B)$ specifically for this van't Hoff ideal special case, in a form that can be used directly in the main article.

When the engine is treated as a static osmometer and volume additivity is assumed for a dilute *Test* solution, the osmotic pressure of the *Test* solution is expressed through its hypothetical hydrostatic pressure equivalent

$$\begin{aligned}\Delta\pi(Test) &= \left(\frac{\Delta V_C^{eq}(Test)}{A_C}\right)\cdot\tilde{\rho}(Test)\cdot\mathbf{g}\\ &= \left(\frac{\Delta V_C^{eq}(Test)}{A_C}\right)\cdot\left(\frac{\rho(Test)\cdot\alpha V_C+\Delta V_C^{eq}(Test)\cdot\boldsymbol{\rho^*(A)}}{\alpha V_C+\Delta V_C^{eq}(Test)}\right)\cdot\mathbf{g}\end{aligned} \tag{S19}$$

Here, $\rho(Test)$ denotes the density of the initial *Test* solution contained in one cylinder, i.e.

$$\rho(Test) = \frac{m_C(Test)}{\alpha V_C} \tag{S20}$$

where $m_C(Test)$ is the mass of *Test* solution initially present in the cylinder volume αV_C. By contrast, $\tilde{\rho}(Test)$ denotes the effective density of the liquid column after osmotic dilution, i.e. the mass-weighted density of the mixture occupying the expanded volume $\alpha V_C + \Delta V_C^{eq}(Test)$

$$\tilde{\rho}(Test) = \frac{\rho(Test)\cdot\alpha V_C+\boldsymbol{\rho^*(A)}\,\Delta V_C^{eq}(Test)}{\alpha V_C+\Delta V_C^{eq}(Test)} \tag{S21}$$

If the osmotic engine is imagined to be equipped with a very large number of cylinders, $\alpha \to 1$, this expression can be further reduced to

$$\Delta\pi(Test) = \left(\frac{\Delta V_C^{eq}(Test)}{A_C}\right)\left(\frac{\rho(Test)\cdot V_C+\Delta V_C^{eq}(Test)\cdot\boldsymbol{\rho^*(A)}}{V_C+\Delta V_C^{eq}(Test)}\right)\mathbf{g} \tag{S22}$$

and, because $\psi = \Delta V_C^{eq}(Test)/\alpha V_C \to \Delta V_C^{eq}(Test)/V_C$ for $\alpha \to 1$, Eq.(S22) can be further simplified to

$$\Delta\pi(Test) = \left(\frac{\psi V_C}{A_C}\right)\left(\frac{\rho(Test)+\psi\cdot\boldsymbol{\rho^*(A)}}{1+\psi}\right)\mathbf{g} \tag{S23}$$

If Eq.(S23) is normalized to the standard pressure

$$\mathbf{P}^\circ = \left(\frac{V_C}{A_C}\right)\cdot\boldsymbol{\rho^*(A)}\cdot\mathbf{g} = 1\,\mathrm{bar}$$

the dimensionless variant of $\Delta\pi(Test)$ is given as

$$\Delta\hat{\pi}(Test) = \frac{\Delta\pi(Test)}{\mathbf{P}^\circ} \tag{S24}$$

Substitution of Eq.(S23) into this definition yields

$$\Delta\hat{\pi}(Test) = \frac{\left(\frac{\psi V_C}{A_C}\right)\left(\frac{\rho(Test)+\psi\cdot\boldsymbol{\rho^*(A)}}{1+\psi}\right)\mathbf{g}}{\left(\frac{V_C}{A_C}\right)\boldsymbol{\rho^*(A)}\mathbf{g}} \tag{S25}$$

which can be reduced to the standard quadratic equation

$$\psi^2 + \left(\hat{\rho}(Test) - \Delta\hat{\pi}(Test)\right)\psi - \Delta\hat{\pi}(Test) = 0 \tag{S26}$$

where $\hat{\rho}(Test)$ is the relative density defined as

$$\hat{\rho}(Test) = \frac{\rho(Test)}{\boldsymbol{\rho^*(A)}} \tag{S27}$$

and where the quadratic Eq.(S26) has the solution

$$\psi = \frac{\Delta\widehat{\pi}(Test) - \widehat{\rho}(Test) + \sqrt{\left(\widehat{\rho}(Test) - \Delta\widehat{\pi}(Test)\right)^2 + 4\Delta\widehat{\pi}(Test)}}{2} \qquad \text{(S28)}$$

In the dilute limit, $\Delta\widehat{\pi}(Test) \to 0$ as $\rho(Test) \to \boldsymbol{\rho^*(A)}$, and Eq.(S28) shows that ψ tends toward $\Delta\widehat{\pi}(Test)$. Thus, for dilute *Test* solutions, it follows that

$$\psi \approx \Delta\widehat{\pi}(Test) = \frac{\Delta\pi(Test)}{\mathbf{P}^\circ} \Rightarrow \Delta V_C^{eq}(Test) \approx \frac{V_C\,\Delta\pi(Test)}{\mathbf{P}^\circ} \qquad \text{(S29)}$$

Note that if the *Test* solution does not satisfy the assumption of volume additivity, the expressions in Eq.(S28) or Eq.(S29) may nonetheless provide an experimenter with practical guidance for designing an experiment, as illustrated in Fig.(9). Because the exhaust volume is recirculated into the *Test* solution, the dimensionless expansion can equivalently be written as

$$\begin{aligned} \psi &= \frac{\Delta V_C^{eq}(Test)}{\alpha V_C} \\ &= \frac{\Delta V^{eq}(Test)}{V(Test)} \\ &\approx \frac{\Delta V^{stop}(Test)}{V(Test)} \quad \text{for} \quad \alpha \to 1 \end{aligned} \qquad \text{(S30)}$$

In the dilute limit, Eq.(S29) therefore generalizes to the total *Test* volume as

$$\Delta V^{eq}(Test) \approx \frac{V(Test)\,\Delta\pi(Test)}{\mathbf{P}^\circ} \qquad \text{(S31)}$$

This relation shows that the osmotic engine can be used in a practically meaningful way also for more concentrated solutions than those that can be conveniently handled by a conventional static osmometer.

Upon implicit differentiation of Eq.(S26) with respect to $n_C(B)$, and subsequent standard algebraic manipulations and abbreviations, the following expression is obtained

$$\frac{\partial\psi}{\partial n_C(B)} = \frac{\left\{\frac{\partial\Delta\widehat{\pi}(Test)}{\partial n_C(B)} - \frac{\partial\widehat{\rho}(Test)}{\partial n_C(B)}\right\}\psi + \frac{\partial\Delta\widehat{\pi}(Test)}{\partial n_C(B)}}{2\psi + \widehat{\rho}(Test) - \Delta\widehat{\pi}(Test)} \qquad \text{(S32)}$$

For theoretical use in the preceding relation Eq.(71), in the section entitled: A Theoretical Perspective, the relation for $n_C(B)\,\frac{\partial\psi}{\partial n_C(B)}$ is required. Multiplication of Eq.(S32) by $n_C(B)$ therefore yields

$$n_C(B)\,\frac{\partial\psi}{\partial n_C(B)} = \frac{\left\{n_C(B)\,\frac{\partial\Delta\widehat{\pi}(Test)}{\partial n_C(B)} - n_C(B)\,\frac{\partial\widehat{\rho}(Test)}{\partial n_C(B)}\right\}\psi + n_C(B)\,\frac{\partial\Delta\widehat{\pi}(Test)}{\partial n_C(B)}}{2\psi + \widehat{\rho}(Test) - \Delta\widehat{\pi}(Test)} \qquad \text{(S33)}$$

Here,

$$\begin{aligned} n_C(B)\,\frac{\partial\Delta\widehat{\pi}(Test)}{\partial n_C(B)} &= n_C(B)\,\frac{\partial}{\partial n_C(B)}\left(\frac{n_C(B)\mathbf{R}T}{V_C(Test)\cdot\mathbf{P}^\circ}\right) \\ &= \Delta\widehat{\pi}(Test) \end{aligned} \qquad \text{(S34)}$$

since $V_C(Test)$ is constant between αV_C and V_C for $\alpha \to 1$. Moreover,

$$\begin{aligned} \frac{\partial\widehat{\rho}(Test)}{\partial n_C(B)} &= \frac{\partial}{\partial n_C(B)}\left(\frac{\rho(Test)}{\boldsymbol{\rho^*(A)}}\right) \\ &= \frac{1}{\boldsymbol{\rho^*(A)}}\,\frac{\partial}{\partial n_C(B)}\left(\frac{n_C(A)\mathbf{M(A)} + n_C(B)\mathbf{M(B)}}{V_C(Test)}\right) \end{aligned} \qquad \text{(S35)}$$

Because $\alpha V_C \le V_C(Test) = n_C(A)\mathbf{V}^*_\mathbf{A} + n_C(B)\mathbf{V}^*_\mathbf{B} \le V_C$, it follows that $V_C(Test) \to V_C$ for $\alpha \to 1$, and hence

$$n_C(B)\,\frac{\partial\widehat{\rho}(Test)}{\partial n_C(B)} = \frac{n_C(B)}{\boldsymbol{\rho^*(A)}\,V_C}\,\frac{\partial}{\partial n_C(B)}\Big(n_C(A)\mathbf{M(A)} + n_C(B)\mathbf{M(B)}\Big) \qquad \text{(S36)}$$

for $\alpha \to 1$, where

$$V_C = n_C(A)\mathbf{V}^*_\mathbf{A} + n_C(B)\mathbf{V}^*_\mathbf{B} \quad \Rightarrow \quad \frac{\partial n_C(A)}{\partial n_C(B)} = -\frac{\mathbf{V}^*_\mathbf{B}}{\mathbf{V}^*_\mathbf{A}} \qquad \text{(S37)}$$

Consequently,

$$\begin{aligned} n_C(B)\,\frac{\partial\widehat{\rho}(Test)}{\partial n_C(B)} &= \frac{n_C(B)}{\boldsymbol{\rho^*(A)}\,V_C}\left(\mathbf{M(A)}\,\frac{\partial n_C(A)}{\partial n_C(B)} + \mathbf{M(B)}\right) \\ &= \frac{n_C(B)}{\boldsymbol{\rho^*(A)}\,V_C}\left(\mathbf{M(B)} - \mathbf{M(A)}\,\frac{\mathbf{V}^*_\mathbf{B}}{\mathbf{V}^*_\mathbf{A}}\right) \end{aligned} \qquad \text{(S38)}$$

When the above relations are combined in Eq.(S33) and the resulting expression is simplified by standard algebraic manipulations, the following result is obtained

$$\begin{aligned} &n_C(B)\,\frac{\partial\psi}{\partial n_C(B)} = \\ &\left(\frac{\Delta\widehat{\pi}(Test)}{\Delta\widehat{\pi}(Test)+1}\right)\cdot\left(\Delta\widehat{\pi}(Test) + 1 + \frac{n_C(B)}{\boldsymbol{\rho^*(A)}\,V_C}\left(\mathbf{M(A)}\,\frac{\mathbf{V}^*_\mathbf{B}}{\mathbf{V}^*_\mathbf{A}} - \mathbf{M(B)}\right)\right) \end{aligned} \qquad \text{(S39)}$$

Because $n_C(B)/\alpha V_C = n(B)/V(Test) = c(B)$, where $c(B)$ is the molar concentration of B in the *Test* solution, it follows that $n_C(B)/V_C = c(B)$ for $\alpha \to 1$, and thus Eq.(S39) can be rewritten for the *Test* solution as

$$\begin{aligned} &n(B)\,\frac{\partial\psi}{\partial n(B)} = \\ &\left(\frac{\Delta\widehat{\pi}(Test)}{\Delta\widehat{\pi}(Test)+1}\right)\cdot\left(\Delta\widehat{\pi}(Test) + 1 + \frac{c(B)}{\boldsymbol{\rho^*(A)}}\left(\mathbf{M(A)}\,\frac{\mathbf{V}^*_\mathbf{B}}{\mathbf{V}^*_\mathbf{A}} - \mathbf{M(B)}\right)\right) \end{aligned} \qquad \text{(S40)}$$

where the factor $\mathbf{V}^*_\mathbf{B}/\mathbf{V}^*_\mathbf{A}$ in Eq.(S40) can be rewritten as

$$\frac{\mathbf{V}^*_\mathbf{B}}{\mathbf{V}^*_\mathbf{A}} = \frac{\mathbf{M(B)}/\boldsymbol{\rho^*(B)}}{\mathbf{M(A)}/\boldsymbol{\rho^*(A)}} \qquad \text{(S41)}$$

and thus it follows that

$$\begin{aligned} &n(B)\,\frac{\partial\psi}{\partial n(B)} = \\ &\frac{\Delta\widehat{\pi}(Test)}{\Delta\widehat{\pi}(Test)+1}\left(\Delta\widehat{\pi}(Test) + 1 + c(B)\cdot\mathbf{M(B)}\left(\frac{1}{\boldsymbol{\rho^*(B)}} - \frac{1}{\boldsymbol{\rho^*(A)}}\right)\right) = \\ &\frac{\Delta\widehat{\pi}(Test)}{\Delta\widehat{\pi}(Test)+1}\left(\Delta\widehat{\pi}(Test) + 1 + \frac{n(B)\cdot\mathbf{M(B)}}{V(Test)}\left(\frac{\boldsymbol{\rho^*(A)} - \boldsymbol{\rho^*(B)}}{\boldsymbol{\rho^*(A)}\cdot\boldsymbol{\rho^*(B)}}\right)\right) = \\ &\frac{\Delta\widehat{\pi}(Test)}{\Delta\widehat{\pi}(Test)+1}\left(\Delta\widehat{\pi}(Test) + 1 + \frac{n(B)\cdot\mathbf{M(B)}}{V(Test)\cdot\boldsymbol{\rho^*(A)}}\left(\frac{\boldsymbol{\rho^*(A)} - \boldsymbol{\rho^*(B)}}{\boldsymbol{\rho^*(B)}}\right)\right) \end{aligned} \qquad \text{(S42)}$$

where the mass of the solvent A in the *Test* solution is approximately equal to $V(Test)\cdot\boldsymbol{\rho^*(A)}$ for a dilute solution of B, and thus the solute B's molality, $m(B)$, is identified as $n(B)/\Big(V(Test)\cdot\boldsymbol{\rho^*(A)}\Big)$. Hence it follows that

$$\begin{aligned} &n(B)\,\frac{\partial\psi}{\partial n(B)} = \\ &\left(\frac{\Delta\widehat{\pi}(Test)}{\Delta\widehat{\pi}(Test)+1}\right)\left(\Delta\widehat{\pi}(Test) + 1 + m(B)\cdot\mathbf{M(B)}\left(\frac{\boldsymbol{\rho^*(A)} - \boldsymbol{\rho^*(B)}}{\boldsymbol{\rho^*(B)}}\right)\right) \end{aligned} \qquad \text{(S43)}$$

For the van't Hoff ideal dilute-limit case considered above, the osmotic expansion factor ψ is related directly to the solvent increment associated with osmotic dilution and osmotic equilibrium. This makes it possible to reformulate the ideal-mixing contribution in terms of the osmotically induced increase in the solvent amount, as shown below. Under strongly idealised conditions, an approximate expression for the osmotic deviation variable $n(A)^{Dil}$ may be derived directly from the equilibrium volume expansion of the *Test* solution. By Eq.(15) and, in the dilute limit, consistently with Eq.(S29), one has at osmotic equilibrium

$$\psi \approx \frac{\Delta\pi(Test)}{\mathbf{P}^{\circ}} \tag{S44}$$

Since ψ is defined as the relative equilibrium volume expansion of the *Test* solution, this may be written as

$$\frac{\Delta V^{eq}}{V(Test)} \approx \frac{\Delta\pi(Test)}{\mathbf{P}^{\circ}} \tag{S45}$$

where $V(Test)$ denotes the volume of the binary *Test* solution consisting of $n(A)$ and $n(B)$ prior to osmotic dilution. It follows that

$$\Delta V^{eq} \approx V(Test) \cdot \frac{\Delta\pi(Test)}{\mathbf{P}^{\circ}} \tag{S46}$$

Hence, in the van't Hoff ideal limit it follows that

$$\Delta V^{eq} = \frac{n(B)\mathbf{R}T}{\mathbf{P}^{\circ}} \tag{S47}$$

The same equilibrium volume change may also be expressed as

$$\Delta V^{eq} = \Delta n(A)\left(\frac{\partial V}{\partial n(A)}\right) + \Delta n(B)\left(\frac{\partial V}{\partial n(B)}\right) \tag{S48}$$

Because the membrane is assumed to be perfectly semipermeable, the solute amount remains unchanged during osmotic equilibration, i.e.

$$\Delta n(B) = 0 \tag{S49}$$

Moreover, by definition, the solvent increment is identified as

$$\Delta n(A) \equiv n(A)^{Dil} \tag{S50}$$

Hence, in the present case

$$\Delta V^{eq} = n(A)^{Dil}\left(\frac{\partial V}{\partial n(A)}\right) \tag{S51}$$

In the dilute limit, $n(B) \to 0$, the partial derivative $\partial V/\partial n(A)$ may, as a first rude approximation, be replaced by the molar volume of the pure solvent, $\mathbf{V}^{*}_{\mathbf{A}}$. One then obtains

$$\Delta V^{eq} \approx n(A)^{Dil} \cdot \mathbf{V}^{*}_{\mathbf{A}} \tag{S52}$$

Combination with the above relation Eq.(S47) gives

$$\frac{n(B)\mathbf{R}T}{\mathbf{P}^{\circ}} \approx n(A)^{Dil} \cdot \mathbf{V}^{*}_{\mathbf{A}} \tag{S53}$$

Since

$$\mathbf{V}^{*}_{\mathbf{A}} = \frac{\mathbf{M(A)}}{\boldsymbol{\rho^{*}(A)}} \tag{S54}$$

it follows that

$$\frac{n(B)\mathbf{R}T}{\mathbf{P}^{\circ}} \approx n(A)^{Dil} \cdot \frac{\mathbf{M(A)}}{\boldsymbol{\rho^{*}(A)}} \tag{S55}$$

and thus

$$n(A)^{Dil} \approx n(B)\left(\frac{\mathbf{R}T}{\mathbf{P}^{\circ}}\right)\left(\frac{\boldsymbol{\rho^{*}(A)}}{\mathbf{M(A)}}\right) \tag{S56}$$

Within this approximation, one immediately obtains

$$\frac{\partial n(A)^{Dil}}{\partial n(B)} \approx \left(\frac{\mathbf{R}T}{\mathbf{P}^{\circ}}\right)\left(\frac{\boldsymbol{\rho^{*}(A)}}{\mathbf{M(A)}}\right) \tag{S57}$$

When the ideal Gibbs free energy of mixing of the osmotically diluted *Test* solution, ΔG^{ref}_{mix}, is considered, as defined in Eq.(23), it follows that

$$\frac{\Delta G^{ref}_{mix}}{\mathbf{R}T} = (n(A) + n(A)^{Dil}) \ln x^{eq}(A) + n(B) \ln x^{eq}(B) \tag{S58}$$

It should be noted that ΔG^{ref}_{mix} constitutes part of the mathematical model used to calculate ΔG_{mix}. Therefore, it is important to analyse

$$\frac{1}{\mathbf{R}T}\frac{\partial \Delta G^{ref}_{mix}}{\partial n(B)} \tag{S59}$$

in order to estimate the activity coefficient of solute B. Thus,

$$\frac{\partial}{\partial n(B)}\Big((n(A) + n(A)^{Dil}) \ln x^{eq}(A) + n(B) \ln x^{eq}(B)\Big) \tag{S60}$$

must be analyzed.

Here, $n(A)^{Dil}$ is interpreted as the osmotic deviation variable, i.e. the additional amount of solvent A transferred into the *Test* solution upon dilution to osmotic equilibrium. The solvent amount in the equilibrated solution is therefore $n(A) + n(A)^{Dil}$, whereas the solute amount remains $n(B)$, consistent with perfect semipermeability. The total amount of substance is

$$n_T = \Big(n(A) + n(A)^{Dil}\Big) + n(B) \tag{S61}$$

so that the mole fractions become

$$x^{eq}(A) = \frac{n(A) + n(A)^{Dil}}{n_T} \tag{S62}$$

and

$$x^{eq}(B) = \frac{n(B)}{n_T} \tag{S63}$$

To this it is noted that, in the section: Energy Balance in the Osmotic Engine, the notation x^{Final}_{A} and x^{Final}_{B} is also used for $x^{eq}(A)$ and $x^{eq}(B)$, respectively. The logarithmic expression may then be rewritten as

$$\begin{aligned} &\Big(n(A) + n(A)^{Dil}\Big) \ln x^{eq}(A) + n(B) \ln x^{eq}(B) = \\ &\Big(n(A) + n(A)^{Dil}\Big) \ln \Big(n(A) + n(A)^{Dil}\Big) + n(B) \ln n(B) - n_T \ln n_T \end{aligned} \tag{S64}$$

For notational convenience, let

$$\eta = n(A)^{Dil} \tag{S65}$$

such that

$$n_T = n(A) + \eta + n(B) \tag{S66}$$

Since the osmotic dilution is induced by the solute, η must in general be regarded as a function of $n(B)$. Differentiation with respect to $n(B)$ therefore requires application of the chain rule. One obtains

$$\begin{aligned} &\frac{\partial}{\partial n(B)}\Big((n(A) + \eta) \ln(n(A) + \eta) + n(B) \ln n(B) - n_T \ln n_T\Big) = \\ &\frac{\partial \eta}{\partial n(B)} \cdot \Big(\ln(n(A) + \eta) + 1\Big) + \ln n(B) + 1 - \frac{\partial n_T}{\partial n(B)} \cdot (\ln n_T + 1) \end{aligned} \tag{S67}$$

Since

$$\frac{\partial n_T}{\partial n(B)} = 1 + \frac{\partial \eta}{\partial n(B)} \tag{S68}$$

this becomes

$$\begin{aligned} &\frac{\partial}{\partial n(B)}\Big((n(A) + \eta) \ln(n(A) + \eta) + n(B) \ln n(B) - n_T \ln n_T\Big) = \\ &\frac{\partial \eta}{\partial n(B)}\Big(\ln(n(A) + \eta) + 1\Big) + \ln n(B) + 1 - \left(1 + \frac{\partial \eta}{\partial n(B)}\right)(\ln n_T + 1) \end{aligned} \tag{S69}$$

After cancellation of the constant terms, this reduces to

$$\begin{aligned} &\frac{\partial}{\partial n(B)}\Big((n(A) + \eta) \ln(n(A) + \eta) + n(B) \ln n(B) - n_T \ln n_T\Big) = \\ &\frac{\partial \eta}{\partial n(B)} \cdot \ln(n(A) + \eta) + \ln n(B) - \left(1 + \frac{\partial \eta}{\partial n(B)}\right) \ln n_T \end{aligned} \tag{S70}$$

Using the definitions of $x^{eq}(A)$ and $x^{eq}(B)$, the derivative may finally be written in the compact form

$$\begin{aligned} &\frac{\partial}{\partial n(B)}\Big(\Big(n(A) + n(A)^{Dil}\Big) \ln x^{eq}(A) + n(B) \ln x^{eq}(B)\Big) = \\ &\frac{\partial n(A)^{Dil}}{\partial n(B)} \ln x^{eq}(A) + \ln x^{eq}(B) \end{aligned} \tag{S71}$$

This expression shows that the derivative contains two distinct contributions. The term $\ln x^{eq}(B)$ is the conventional ideal-mixing contribution associated with the solute. The second term

$$\frac{\partial n(A)^{Dil}}{\partial n(B)} \cdot \ln x^{eq}(A) \tag{S72}$$

arises because the solvent amount is not constant, but varies through osmotic dilution: A change in $n(B)$ therefore affects the expression both directly through the solute contribution and indirectly through the solvent contribution via the dependence of $n(A)^{Dil}$ on $n(B)$.

Insertion of the approximate result

$$\frac{\partial n(A)^{Dil}}{\partial n(B)} \approx \left(\frac{\mathbf{R}T}{\mathbf{P}^\circ}\right)\left(\frac{\boldsymbol{\rho^*(A)}}{\mathbf{M(A)}}\right) \tag{S73}$$

then yields

$$\begin{aligned} &\frac{\partial}{\partial n(B)}\Big(\Big(n(A)+n(A)^{Dil}\Big)\cdot \ln x^{eq}(A) + n(B)\cdot \ln x^{eq}(B)\Big) \approx \\ &\qquad\qquad \left(\frac{\mathbf{R}T}{\mathbf{P}^\circ}\right)\left(\frac{\boldsymbol{\rho^*(A)}}{\mathbf{M(A)}}\right)\ln x^{eq}(A) + \ln x^{eq}(B) \end{aligned} \tag{S74}$$

Hence, it follows that

$$\frac{\partial \Delta G^{ref}_{mix}}{\partial n(B)} \approx \mathbf{R}T \cdot \left(\left(\frac{\mathbf{R}T}{\mathbf{P}^\circ}\right)\left(\frac{\boldsymbol{\rho^*(A)}}{\mathbf{M(A)}}\right)\ln x^{eq}(A) + \ln x^{eq}(B)\right) \tag{S75}$$

to which it is noted that

$$\begin{aligned} &\ln x^{eq}(B) \to \ln x(B) &&\text{for} \quad n(B)\to 0 \\ &\ln x^{eq}(A) \to \ln x(A) = 0 &&\text{for} \quad n(B)\to 0 \end{aligned} \tag{S76}$$

and like this it follows, that in the dilute area

$$\frac{\partial \Delta G^{ref}_{mix}}{\partial n(B)} \to \mathbf{R}T \cdot \ln x(B) \qquad \text{for} \qquad n(B)\to 0 \tag{S77}$$