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The Source

Substitution-Initiated Self-Separation of the Substituted-Chrysene Stock from a Polyaromatic Bulk, and the Supply It Delivers to the Protocell

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Abstract

The protocell articles take their substituted-chrysene stock as a boundary condition. Article 77 admits the 6,12-, 3,6,12- and 3,6,9,12-substituted families and places their manufacture, enrichment and self-separation outside its problem; Article 65 reduces the steady cycle to an inequality on a pool rate it does not supply; Article 40 records that an infinite admissible distance does not imply a physical scission, and states the dynamical scission theorem as a target. This paper supplies the source upstream of all three.

Chrysene in a polyaromatic bulk is brominated, the 6- and 12-positions first and together and the 3-position next, as the filing's experiment reports; each bromine is replaced through an oxalate and reduced to a hydroxyethoxy arm; each polar arm lowers the unit's transfer free energy out of the bulk, so separation is initiated by substitution. We model the bulk as a finite absorbing chain on the substitution degree, prove the exit distribution in closed form, and show that one design equation, $k_3 = e_2(R_T/R_D)(1 + e_3/k_4)$, matches the exported stream to the protocell's demand at efficiency 0.998437 in the illustration. The fast fourth step this requires is a stated design requirement, priced against initiator loss by $k_4/k_3 = q\rho^*/(x(1 + x))$ with $x = e_3/k_4$: the illustration asks 18,511, and tolerating five per cent of surplus initiator lowers that to 18.5.

Selectivity against the polyaromatic background does not rest on the arming step being selective, and a second filter of a different kind is what makes that so. The exported units stack into columns, and because the four substitution positions sit on a core of C_{2h} symmetry the arms of one unit fall over the arms of the next, so a column carries continuous arm registrations; a guest that cannot present the pattern breaks ν of them at each of two contacts and is excluded by $e^{-2\nu\Delta_{\mathrm{rgy}}}$. Article 40's enumeration of the four-ring polyhexes denies the pattern to every four-ring competitor. Partition, which acts on solvation, cannot discriminate an armed competitor from an armed chrysene at the same arm count; registry, which acts on geometry, can, and it is what protects the disubstituted stream. An unselective arming reagent therefore raises the stock-phase impurity concentration, in which the column bound is linear, and changes nothing structural.

With returns disallowed the bulk empties exponentially, the admissible stock retains weight 0.998901, and the exports of degree below two form a dynamically isolated waste class, discharging Article 40's Target 49 for this realisation in the classical sector. Article 77's predicate, which admits by substitution family and full specification, already accommodates every arm the source makes, so no widening and no arm-scheduling hypothesis is required. The supply interface adds a demand vector, a throughput in expectation, an upstream carbon ledger in which the oxalate is the only incorporated carbon reagent, and a necessary condition for diffusion-limited delivery.

Keywords: Chrysene Formalism; substituted chrysene; bromination; oxalate; self-separation; absorbing Markov chain; M-matrix; isodesmic aggregation; dynamical scission; material supply; protocell.

1 Introduction

1.1 The purity problem

A protocell needs nucleic acids, phospholipids and amino-acid residues together, in one compartment, at the same time. Each of the three has prebiotic routes, and each route asks for its own precursors at its own concentration, in a medium that does not consume them first. Article 77 surveys the experimental state of that programme [Sch26a, §1]: nonenzymatic template copying inside fatty-acid vesicles, coupled vesicle growth and

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division, peptide synthesis that promotes membrane growth, and, as a common-source objective, cyanosulfidic networks that connect precursors of all three through one chemistry. What the survey also shows is how much has to be arranged at once. Even reconciling two of the requirements can take a specific mediator, as citrate does for magnesium-dependent copying inside a fatty-acid membrane.

The usual setting for these routes is a mixture: a melt, a pond, a vent effluent, a meteoritic extract. Such a mixture supplies a great many species, each at a small fraction, and the difficulty is not that the wanted species are absent but that they are dilute and are accompanied. Two distinct things must therefore be arranged, and they are not the same thing.

- *Concentration.* The wanted species must be present at an activity at which its reaction competes with its loss. Dehydration–rehydration cycling, thermal pores and coacervate droplets all address this, and they address it well.
- *Purity.* The wanted species must be accompanied by few enough competitors that the reaction it is meant to undergo outruns the ones it is not. Nothing in a concentrating mechanism supplies this: a cycle that evaporates a pond, a pore that accumulates solute by thermophoresis and a droplet that partitions a polyanion all concentrate what is there, the competitors included, and some of them enrich the competitors preferentially.

The two scale against each other as the number of required species grows. A route that needs m specific precursors simultaneously requires all m to be concentrated and mutually compatible in the same place, and the fraction of a random mixture that satisfies that falls steeply in m, while the number of possible cross reactions rises as m^2. This is the structural form of the difficulty, and it is why "a primordial soup contained the ingredients" is a weaker premise than it appears: a mixture that contains everything is, for this purpose, a mixture that contains nothing in particular.

Scholium 1.1. The position this paper takes, and it is a position rather than a survey finding, is that purity is the harder of the two requirements and the one least addressed. Concentration has several demonstrated mechanisms, of which Article 77's survey names three; selective enrichment of one species against a chemically similar background is not among the things those mechanisms do, and this paper cites no mechanism that does it. Whether the literature contains one is not assessed here. A reader who ranks the two difficulties differently, or who knows of such a mechanism, can read what follows as addressing one difficulty among several, without any result changing.

The corpus answers the first half of this by collapsing the requirement. The architecture of Articles 62, 65, 77 and 78 draws its nucleobases, its membrane lipid, its amino-acid residues and its interior lattice from one aromatic skeleton in three substitution patterns, so what must be supplied is not m unrelated precursors but one species in three forms, together with carbon-free heteroatoms and, here, the oxalate that carries the arm carbon. Article 65 makes this exact: the architecture's whole input requirement is three chrysene species and a heteroatom feedstock, four species it consumes and does not make [Sch26d, Thm. 7.3]. The cross-reaction count collapses with m, and the concentration requirement becomes a requirement on one pool.

That leaves the second half, and it is the question this paper addresses. One species at sufficient purity is a weaker demand than many, but it is not a free one: the species still has to be got out of the mixture that contains it. The answer proposed here is that it need not be got out by anything external, because the step that prepares it is the step that removes it. A chrysene brominated and armed in the bulk is no longer the molecule that was at home there; each polar arm lowers its transfer free energy out of the hydrophobic phase, so the act of making the reagent is the act of separating it. Purification is not a stage that must be arranged before the chemistry starts; it is a by-product of the chemistry itself, and the degree of substitution that makes a unit useful downstream is the same quantity that makes it leave.

Taken alone that would only displace the difficulty, since a competitor that is also armed also leaves. What closes the argument is that the departure is followed by a second filter of a different kind. The units that have left do not remain as free molecules; they stack, face to face, into columns, and because the four substitution positions sit on a core of C_{2h} symmetry the arms of one unit fall over the arms of the next, so a column carries continuous arm registrations along its length. A guest that cannot present that pattern interrupts them all, at both of its contacts, and is excluded by a factor exponential in their number. Among the four-ring polyaromatics the pattern is not available to anything else: Article 40's enumeration finds exactly seven, of which exactly one has the reference symmetry, and that one is chrysene. The first filter works on solvation and does not distinguish an armed competitor from an armed chrysene at the same arm count; the second works on geometry and does. Neither has to be perfect, because they multiply.

Scholium 1.2. What this does and does not resolve should be said plainly at the outset, because the argument above is the motivation and not a theorem. Three things are assumed rather than shown. That chrysene is present in the bulk at some nonzero fraction is an input (Hypothesis 4.15); nothing here produces it. That a registration is worth a free energy Δ_{rgy} which is positive and not small is a hypothesis (Hypothesis 8.5), and it is the premise the second filter rests on entirely; no value is supplied. And the uniqueness that denies the pattern to competitors is proved over the *four-ring* polyaromatics only (Proposition 4.4), so a species of another ring count is outside it.

What is *not* assumed is worth naming too, because an earlier form of this paper assumed it. The arming step need not be selective. If the bromination and the oxalate substitution act on the rest of the polyaromatic background as readily as on chrysene, those competitors are armed, they partition out of the bulk alongside the stock, and the only consequence is that the impurity concentration in the stock phase rises: the bound of Proposition 8.11 is linear in it and the registry factor is

untouched. The requirement that a random mixture be selectively enriched has not been met by assuming a selective reagent; it has been moved onto a geometric property of the stack, where Proposition 4.4 bounds the competitors by enumeration and Corollary 8.6 prices the exclusion. What remains to be measured is one free energy.

1.2 What the corpus leaves upstream

Three places in the corpus stop at the same boundary from different sides.

The carbon-traceable protocell. Article 77 admits "specified members of three main substitution families" and states that their "manufacture, progressive enrichment and self-separation ... are outside the problem" [Sch26a, §3]. Its Proposition 9.3 shows that no productive cycle is periodic without an admitted replenishment; the replenishment is not constructed there.

The material ledger. Article 65 proves that a steady cycle requires a pool rate of disubstituted units $R \geq 5L + \frac{\alpha}{1-\alpha}N + \nu L$ per period [Sch26d, Thm. 8.5] and leaves the rate as its Target 12.2.

The twelve-axiom foundation. Article 40, the second restatement of the formalism and the one that supersedes the earlier axiomatic Article 2 [Sch26b], records the non-implication $d^*_{\mathfrak{C}}(x, y) = +\infty \not\Rightarrow$ autonomous physical scission, and states as a target a dynamical scission theorem in which a rejected component is removed, absorbed or dynamically isolated [Sch26c, Thm. 49].

The monograph. Chapter 2 of the fifth volume [Sch26f] describes the thermodynamic topological purification (its §2.8.1) of the substituted chrysene from a degenerate polyaromatic conglomerate. Its narrative motivates this paper; Section 13 rules on its theorems individually.

1.3 What this paper addresses

(i) What, in a polyaromatic bulk, makes a substituted chrysene leave, and at which degree (Sections 4–6).
(ii) Whether the exported stream can have the composition the protocell needs, which is dominated by the 6,12-disubstituted unit, and at what efficiency and what kinetic cost (Section 7).
(iii) In what precise sense the separation is irreversible, and what that costs in premises (Section 9).
(iv) What the source delivers across the boundary of Articles 65, 77 and 78 (Section 10).

1.4 What is established here, by kind

Recovered. Article 40's classification of the four-ring polyhexes (Thm. 51, Props. 53–54, Thm. 55, Cor. 8) and the narrowed scope of the former "Chrysene Isomorphism Theorem" (§9.10, Rem. 44); Article 65's demand (Thm. 8.5) and documentary bundle; Article 78's ICL supply and bilayer demand (eq. (1), Prop. 9.1); Article 77's admission predicate, formula, reservations and open balance (§3, Props. 3.2, 3.10, 3.12, Thm. 3.5); Article 40's A12 structure and non-implications; the filing's bromination sequence (Fig. 12 and its description).

Proved here. Partition ordering and purity at frozen composition (Thm. 5.1, Prop. 5.3); exit distribution (Thm. 6.4); off-chain leakage (Prop. 6.5); axis-selectivity window (Thm. 6.7); completion identity (Prop. 6.9); the pattern unavailable to a four-ring competitor (Cor. 4.5); registry suppression (Cor. 8.6); design equation, efficiency and the cooperativity trade-off (Thms. 7.2, 7.3, Prop. 7.5); low-conversion crossing (Prop. 7.9); column impurity and buffering (Thms. 8.3, 8.8); dynamical scission with returns disallowed (Thm. 9.4, Cor. 9.5); what returns would do (Props. 9.7, 9.8); supply in expectation (Thm. 10.3); admission independent of the arm law (Thm. 10.7); formula with oxalate and phosphate arms (Prop. 4.8); upstream carbon ledger (Prop. 10.13); a necessary condition for delivery (Prop. 10.15).

Found. Under the author's kinetics the source matches the demand with waste of order 10^{-3} (Cor. 7.4); the price is a fast fourth step whose required size falls steeply as initiator loss is tolerated (Prop. 7.5). The D-rich composition is stable only because admitted units do not return (Prop. 9.7). Article 77's predicate needs no widening (Rem. 10.6, Thm. 10.7). Selectivity against the background is three mechanisms acting on different properties, of which only the first has an experimental anchor and only the third protects the disubstituted stream (Scholium 8.14).

Computed. Blocks V1–V12 of Appendix B.

Supposed. Appendix A; the chemical premises carry documentary marks.

Not claimed. Proposition 3.1.

2 Status, nomenclature, scope

Convention 2.1 (Status labels)**.** [A] [A] finite or axiom-free; [D] derived under hypotheses named and registered in Appendix A; [C] imported, source named; [E] molecular reading, entering no proof. Scholia are unlabelled and enter no proof.

Convention 2.2 (Patent citation and documentary marks)**.** [A] Adopted from Article 65 [Sch26d, Convs. 2.2–2.3]: the filing [Sch25] is cited through Article 65's documentary bundle H_{mat}, as amended by Ruling 13.6 to add clause (i) for Fig. 12; a sentence quoting the filing is [E]; a chemical premise carries the mark A (attested by a clause of the bundle), S (stated by the author) or B (to be discovered). No theorem rests on a B entry.

Convention 2.3 (Carbon boundary and admission)**.** A The source sits upstream of Article 77's admission boundary. Admission occurs at export: a unit whose substitution set is one of Article 77's families is admitted when it enters the stock phase, receiving fresh origin labels [Sch26a, Def. 3.3], together with the constitutional record its Definition 3.1 requires. Admitted units do not return to the bulk (Hypothesis 4.18), so no admitted carbon is modified by the source and no core is admitted twice, as Article 77's boundary requires. Exports of degree 0 or 1 lie in no family; they are not admitted and form the isolated waste class $\mathcal{W}$ (Definition 9.1). Every carbon of an admitted unit is traced to a chrysene core drawn from the bulk or to the oxalate reagent (Definition 4.7).

Convention 2.4 (Seniority)**.** A Where this paper and an earlier article speak to the same object, Section 13 states which governs. Nothing earlier is amended silently.

Notation 2.5. $\Lambda = \{3, 6, 9, 12\}$; $n \in \{0, \dots, 4\}$ the number of installed oxygen arms (the degree); β bulk, σ stock phase, κ its columnar sub-phase; k_n advance rates, e_n export rates, q per-arm partition enhancement; D, I, T the 6,12-, 3,6,12- and 3,6,9,12-substituted units (Article 65 notation); R_D, R_I, R_T per-period demands; Φ bulk throughput in chrysene units per period; $\rho^* = R_D/R_T$; η material efficiency. Tolerances are written ε.

3 Non-implications

Proposition 3.1 (Non-implications)**.** A *None of the following is asserted.*

(i) No abundance claim. *That a polyaromatic bulk contains chrysene, or chrysene at any fraction (Hypothesis 4.15).*

(ii) No rate derived. *The bromination sequence and the species are attested by the filing's experiment (clause (i) of Ruling 13.6); its rate magnitudes, those of the oxalate substitution and the reduction, and the export rates are not derived. Every magnitude in the verification blocks is a stipulated illustration.*

(iii) No setting attested. *The filing's bromination was run in solution; clause (i) attests the sequence, not its occurrence in a polyaromatic bulk.*

(iv) No purity of one. *Every purity statement is a bound strictly below one at finite parameters.*

(v) No topological irreversibility. *The irreversibility proved here rests on covalent substitution (Hypothesis 4.17) and on the stipulation that admitted units do not return (Hypothesis 4.18), not on membership in a K-theoretic summand or on an infinite distance.*

(vi) No scission from admissibility. *Article 40's display $d^*_{\mathfrak{C}} = +\infty \nRightarrow$ autonomous physical scission [Sch26c, §1] and its non-implication $C_j \geq \tau_j \nRightarrow$ automatic removal [Sch26c, eq. (442)] are honoured; every removal is proved from a stated dynamics.*

(vii) No separation without the no-return premise. *Proposition 9.7 shows what a source with returns would do instead.*

(viii) No thermodynamic minimum. *That the 3,6,9,12 pattern is a global free-energy minimum of substitution. Here it is the terminal degree of a kinetic chain.*

(ix) No geometric-to-kinetic inference. *That Axiom A3's inequivalence of the two attachment directions implies the rate order of Hypothesis 7.1. A3 permits it and does not supply it.*

(x) No realised supply. *That any environment delivers the throughput of Theorem 10.3. That theorem converts Article 65's Target 12.2 into conditions on bulk parameters; it does not meet them.*

(xi) No identification of the binding delivery step. *Proposition 10.15 gives a necessary condition only.*

Scholium 3.2. Items (v) and (vi) come first because the monograph's account of purification rests on the two inferences they refuse. The account is not discarded; its content is moved from the metric to the dynamics, which is where Article 40 says it must live, and the one ingredient the dynamics cannot supply by itself—that admitted units stay admitted—is stated as a premise rather than concealed in a metric.

4 Objects

4.1 Substitution sets and their orbits

Definition 4.1 (Substitution set)**.** A A *substitution set* is a subset $S \subseteq \Lambda$; its *degree* is $|S|$. The chain

$$\mathcal{P} : \varnothing \subset \{6\} \subset \{6, 12\} \subset \{3, 6, 12\} \subset \{3, 6, 9, 12\}$$

extends the monograph trajectory [Sch26f, §2.2.2], which begins at $\Psi_{6,12}$, by its two first steps; $D = \{6, 12\}$, $I = \{3, 6, 12\}$, $T = \{3, 6, 9, 12\}$.

Lemma 4.2 (Orbits under the reference symmetry)**.** A *Let ι be the inversion of the C_{2h} reference of Axiom A2, acting on the locants of Axiom A3 (eqs. (52)–(53) there) by $3 \leftrightarrow 9$, $6 \leftrightarrow 12$ [Sch26c]. The sixteen subsets of Λ fall into ten $\langle\iota\rangle$-orbits. Along $\mathcal{P}$ the number of sites available for the next*

step is $2, 1, 2, 1$*, so under site-independent intrinsic rates the chain rates carry statistical factors* $k_1 = 2\theta_y$*,* $k_2 = \theta'_y$*,* $k_3 = 2\theta_x$*,* $k_4 = \theta'_x$*.*

Proof. Burnside: ι fixes a subset iff it is a union of the orbits $\{3, 9\}$, $\{6, 12\}$, so four subsets are fixed and $(16 + 4)/2 = 10$. The site counts are read off $\mathcal{P}$; $\{6, 9, 12\} = \iota\{3, 6, 12\}$, so both third-step products are the one orbit I. □

Remark 4.3. [A] I is not ι-invariant; a unit carrying it is C_s. A separation criterion based on C_{2h} symmetry would expel the intermediate the monograph retains; the criterion here is the arm count (Ruling 13.4).

4.2 The competitor set

What else the bulk offers decides how hard separation is. Article 40 bounds one part of that set exactly.

Proposition 4.4 (Classification of the four-ring polyhexes)**.** [C] *Up to translation, rotation and reflection of the hexagonal tiling there are exactly seven connected four-cell polyhexes* $S_1, \dots, S_7$ *[Sch26c, Thm. 51]. Of the seven, exactly one—*S_4*—has reference three-dimensional point group* C_{2h} *[Sch26c, Table 1, Prop. 53], and its carbon graph is graph-isomorphic to the externally identified chrysene connectivity graph [Sch26c, Prop. 54]. Hence the canonical carbon framework of every full twelve-axiom model is polyhex-congruent to chrysene [Sch26c, Thm. 55, Cor. 8].*

Corollary 4.5 (The pattern is not available to a four-ring competitor)**.** [D] *No four-ring polyhex other than chrysene carries four peripheral positions on which an inversion of the reference point group acts as* $3 \leftrightarrow 9$*,* $6 \leftrightarrow 12$ *(Lemma 4.2). Within that class the locant structure used throughout this paper therefore singles chrysene out by enumeration rather than by preference, and a competitor armed at four positions cannot present the pattern* Λ *carries.*

Proof. The action in Lemma 4.2 is that of the inversion of a C_{2h} reference (Axiom A2); by Proposition 4.4 no other member of $S_1, \dots, S_7$ has that reference group. □

Remark 4.6 (Scope, and a name that has narrowed)**.** [C] Two limits belong with the import. First, the enumeration is over *four-cell* polyhexes: a polyaromatic bulk holds species of other ring counts, about which Proposition 4.4 says nothing. It bounds one slice of $\mathcal{D}$, not $\mathcal{D}$. Second, Article 40 narrows the phrase "Chrysene Isomorphism Theorem", which an earlier formalism used for a larger bundle of geometric and quantum claims, to the molecular characterization result quoted here, and records that the result does not by itself establish the transfer, field, metric or scission statements the older name carried [Sch26c, §9.10, Rem. 44]. Nothing below uses more than Proposition 4.4 states.

4.3 The source chemistry

Definition 4.7 (Arm installation)**.** [D] Documentary marks in brackets; clause (i) is that of Ruling 13.6.

(a) *Bromination* [A, clause (i)]: electrophilic bromination by Br_2 at the positions of Λ, sequentially, the 6- and 12-positions first and together and the 3-position next.

(b) *Oxalate substitution* [oxalate arm A, clause (i); reagent and rate S]: replacement of each bromine by the oxalate monoester arm $o = -O{-}C(=O){-}C(=O)OH$, the oxalate drawn from solid calcium oxalate CaC_2O_4.

(c) *Reduction* [S]: reduction of o to the hydroxyethoxy arm $e = -O{-}CH_2{-}CH_2{-}OH$ by a carbon-free reductant.

(d) *Cleavage* [S]: cleavage of the aryl ester of an o-arm leaves the phenol arm $h = -OH$ and releases its two carbons as a coproduct.

(e) *Phosphorylation* [A for the phosphorylated catalyst, clause (i); its use S]: downstream of admission, $e \mapsto e_P = -O{-}CH_2{-}CH_2{-}O{-}P(=O)(OH)_2$, the form used for the transformation and for other downstream functions of the protocell.

The arm alphabet is $\mathcal{A} = \{h, o, e, e_P\}$, each a specified finite arm graph in the sense of [Sch26a, Def. 3.1]. The degree n counts installed oxygen arms; a brominated position carrying no arm does not count.

Proposition 4.8 (Formula)**.** [A] *A unit with* n_h, n_o, n_e, n_P *arms of types* h, o, e, e_P *has neutral formula*

$$C_{18+2(n_o+n_e+n_P)}\, H_{12+4n_e+5n_P}\, O_{n_h+4n_o+2n_e+5n_P}\, P_{n_P}.$$

Reduction $o \to e$ *adds* H_4 *and removes* O_2*; phosphorylation* $e \to e_P$ *adds* HO_3P*; neither changes the carbon count. The bis-oxalate D unit is* $C_{22}H_{12}O_8$ *and the fully phosphorylated T unit is* $C_{26}H_{32}O_{20}P_4$*.*

Proof. Each arm replaces one core hydrogen of $C_{18}H_{12}$: h adds net O, o net C_2O_4, e net $C_2H_4O_2$ [Sch26a, Prop. 3.2], and e_P net $C_2H_5O_5P$ by Article 77's monoester balance

$$ROH + H_3PO_4 \longrightarrow ROP(=O)(OH)_2 + H_2O$$

[Sch26a, §3.1]. Differences of these give the two transformations. V7 checks the formula against Article 77's Table 2 and both balances at every arm count. The neutral-acid forms

are a bookkeeping convention; charge and counterions are additional data. □

Hypothesis 4.9 (H_{seq}, arm installation is prompt)**.** D S. Oxalate substitution and reduction at a brominated position are fast compared with the next bromination and with export, so the degree advances at the bromination rates and the exported arm is e (or h where cleaved). If the reduction is instead slower than export, units leave carrying o-arms; they are admissible all the same and are reduced downstream, and by Proposition 4.8 the carbon count is unchanged.

Hypothesis 4.10 (H_{cat})**.** D S. The substitution of an aryl bromide by oxalate proceeds at the rates required; any catalyst or solvent is carbon-free, or is declared with its carbon kept out of the products.

Hypothesis 4.11 (H_{sel}, optional)**.** D S, and *not required by any result below*. The non-chrysene polyaromatics of the bulk are not armed on the horizon considered: they are brominated more slowly than chrysene's 6- and 12-positions, or their brominated forms are not converted.
Where it is assumed it is named; where it is not, the competitor concentration in the stock phase, c_d^{σ}, simply takes whatever value the arming leaves it, and the results are stated in that variable. H_{sel} therefore sets a magnitude and not a structure: it lowers c_d^{σ}, and Proposition 8.11 is linear in c_d^{σ}. What keeps an armed competitor out of the stock is not this hypothesis but the two filters that act after export—admission, which refuses any core that is not a chrysene in one of Article 77's families (Theorem 10.7), and registry, which suppresses incorporation into the columns by $e^{-2\nu\Delta_{\text{rgy}}}$ (Corollary 8.6). Scholium 8.14 sets out what each filter is worth.

Hypothesis 4.12 (H_{arm})**.** D S. An installed e-arm keeps its identity on the horizon: no dealkylation $e \to h$ and, after phosphorylation, no monoester hydrolysis $e_P \to e$ before use. Aryl monoesters hydrolyse faster than alkyl ones, so the premise is weaker for h_P than for e_P.

4.4 The bulk and the stock phase

Definition 4.13 (Source system)**.** D (a) A *bulk* β: a hydrophobic polyaromatic phase holding N_0 unsubstituted chrysene units and $N_{\mathcal{D}}$ units of other polycyclic species $\mathcal{D}$. (b) A *stock phase* σ adjacent to β, with a columnar sub-phase $\kappa \subseteq \sigma$ of π-stacked units. (c) Reagents in β at fixed activities over the horizon: Br_2; oxalate, buffered by solid CaC_2O_4; a carbon-free reductant. (d) In the open source, a delivery channel removing admitted units from $\sigma \cup \kappa$ to the protocell.

Hypothesis 4.14 (H_{phase})**.** D S. σ is a volumetric aqueous phase in which free stock monomers and their columnar aggregates are dissolved, and β is mobile enough for reagent transport and for transfer free energies to be additive in arms. Propositions 5.3, 8.11 and 10.15 and Theorem 8.8 use it; a lamellar or purely interfacial σ would invalidate the volume ratio, the molar stacking constant and the three-dimensional diffusion estimate alike.

Hypothesis 4.15 (H_{in})**.** D β contains unsubstituted chrysene at a nonzero fraction $x_0 = N_0/(N_0 + N_{\mathcal{D}})$; results are stated as functions of it.

Hypothesis 4.16 (H_{loc})**.** D All substitution occurs in β; a unit in $\sigma \cup \kappa$ is not further substituted.

Hypothesis 4.17 (H_{cov})**.** D Substitution is covalent and irreversible on the horizon considered: the degree of a unit never decreases.

Hypothesis 4.18 (H_{ret}, no return)**.** D S. An *armed* chrysene unit that has entered σ does not return to β: $r_n = 0$ for $n \geq 1$. This is what Convention 2.3 requires of admitted material, and Proposition 9.7 says what fails without it. It is asserted of armed units only: unsubstituted chrysene and the members of $\mathcal{D}$, which carry no polar arm, partition reversibly, which is what H_{leq} and the equilibrium of Proposition 5.3 use.

4.5 Transfer free energy and export rates

Definition 4.19 (Partition)**.** A For a species s, $\Delta\mu_s = \mu_s^{\sigma} - \mu_s^{\beta}$ is the standard transfer free energy referred to the free monomer in σ, and $P_s = \exp(-\Delta\mu_s/k_BT)$ at dilute ideality. Aggregation in κ is a further sink and is not part of P_s.

Hypothesis 4.20 (H_{add}, thermodynamics)**.** D $\Delta\mu_{(S,a)} = \Delta\mu_0 + \sum_{\ell \in S} \delta_{a(\ell)}$ with every $\delta < 0$. For one arm type, $q = \exp(-\delta/k_BT) > 1$ and $P_n = P_0 q^n$. The theorems use only the ordering and the ladder; whether four arms make e_n large enough for export to compete at all is a separate requirement on magnitudes (Target 14.2).

Hypothesis 4.21 (H_{trans}, from partition to rates)**.** D S. The barrier to re-entering β is independent of the arm count, so the whole partition ladder falls on the forward rate: $e_n = e_0 q^n$. Theorems 6.4, 7.2 and 7.3 hold for general e_n; the window, the bottleneck bound and the cooperativity identity use the ladder.

Hypothesis 4.22 (H_{bulk}, optional)**.** D Under H_{sel}, every $d \in \mathcal{D}$ carries no polar arm, so $P_d \le P_0$. Like H_{sel} it is optional and is named where used: Theorem 5.1's comparison with $\mathcal{D}$ and Proposition 5.3 use it; the chrysene ladder, Theorem 8.3 and Proposition 8.11 as restated do not.

Scholium 4.23. H_{add} with H_{trans} is the "self" in self-separation: substitution changes the unit, and the changed unit's own solvation carries it out. What selects the chrysene is the bromination sequence with H_{sel}; at the stock phase, Article 77's admission by family and the stacking selectivity of Theorem 8.3 select again.

5 Equilibrium partition

Theorem 5.1 (Ordering)**.** D *Under H_{add}, $P_0 < P_1 < P_2 < P_3 < P_4$. If in addition H_{bulk} holds, then $P_d \le P_0$ for every $d \in \mathcal{D}$, so the whole of $\mathcal{D}$ lies below the chrysene ladder.*

Proof. $P_{n+1}/P_n = q > 1$ by H_{add}; the second clause is H_{bulk}. □

Remark 5.2. A Only the first clause is used downstream. An armed competitor has polar arms of its own and no reason to satisfy $P_d \le P_0$: it partitions out of the bulk much as an armed chrysene does. That is why the separation does not rest on the second clause, and why the filters that matter act after export rather than at it.

Proposition 5.3 (Single-stage purity at frozen composition)**.** D *Assume H_{bulk}. Hold the composition fixed, with no substitution running, and let partition equilibrate: $v = V_\sigma/V_\beta$ (H_{phase}), N_n units of degree n, $N_{\ge 2} = \sum_{n\ge 2} N_n$. The fraction* P *of degree-≥ 2 units among the units in σ obeys*

$$1 - \mathsf{P} \;\le\; (1 + vP_2)\,\frac{q^{-2}(N_{\mathcal{D}} + N_0) + q^{-1}N_1}{N_{\ge 2}}.$$

Proof. The fraction of species s in σ is $f_s = vP_s/(1 + vP_s)$, increasing in P_s, and for $x \le y$, $f(x)/f(y) = (x/y)(1 + vy)/(1 + vx) \le (x/y)(1 + vy)$. Hence $f_d \le f_0 \le q^{-2}(1 + vP_2) f_2$ and $f_1 \le q^{-1}(1 + vP_2) f_2$, while $\sum_{n\ge 2} N_n f_n \ge N_{\ge 2} f_2$. Divide. □

Remark 5.4. A One equilibrium stage purifies only if $q^2 \gg N_{\mathcal{D}}/N_{\ge 2}$. The columnar stage supplies an independent second factor (Proposition 8.11). The composition cannot in fact be held fixed while substitution runs; Proposition 9.7 describes the relaxation this bound abstracts from.

6 Substitution-initiated export

Hypothesis 6.1 (H_{reg})**.** D Substitution proceeds along $\mathcal{P}$; from each state, off-chain substitution occurs at rate $\omega_n \le \epsilon_{\text{off}} k_{n+1}$. Documentary marks: the three species A (clause (a) of H_{mat}); the 6,12-then-3 bromination order A (clause (i)); the 9-position as the fourth step, and ϵ_{off}, S.

Definition 6.2 (The export chain)**.** D A chrysene unit in β is a continuous-time Markov chain on transient states $\{0, \dots, 4\}$ (degree) with absorbing states $X_0, \dots, X_4$ (exported at degree n). From n it moves to $n + 1$ at rate k_{n+1} ($k_5 := 0$) and to X_n at rate $e_n > 0$. Its generator on the transient states is the upper bidiagonal matrix

$$G = \begin{pmatrix} -\lambda_0 & k_1 & & & \\ & -\lambda_1 & k_2 & & \\ & & -\lambda_2 & k_3 & \\ & & & -\lambda_3 & k_4 \\ & & & & -\lambda_4 \end{pmatrix}, \qquad \lambda_n = e_n + k_{n+1}.$$

Export is absorbing, by H_{ret}; Proposition 9.7 treats the alternative.

Lemma 6.3 (Triangular spectrum)**.** A *The eigenvalues of G are $-\lambda_0, \dots, -\lambda_4$, all negative.*

Proof. A triangular matrix has its diagonal as spectrum; $\lambda_n \ge e_n > 0$. □

Theorem 6.4 (Exit distribution)**.** A *Started at degree 0,*

$$p_n := \mathbb{P}(\text{exit at degree } n) = \frac{e_n}{\lambda_n} \prod_{j=0}^{n-1} \frac{k_{j+1}}{\lambda_j}, \qquad \sum_{n=0}^{4} p_n = 1,$$

$$\mathbb{E}[\tau_\beta] = \sum_{n=0}^{4} \frac{1}{\lambda_n} \prod_{j<n} \frac{k_{j+1}}{\lambda_j}.$$

Proof. From n the two competing exponential clocks ring first with probabilities e_n/λ_n (export) and k_{n+1}/λ_n (advance); the product is the probability of reaching n. The sum telescopes because $k_5 = 0$ forces exit from degree 4. Each visit to n lasts $\mathrm{Exp}(\lambda_n)$. Block V1 checks the closed form against the fundamental-matrix solution $(I - Q)^{-1}R$ of the embedded chain [KS60] in exact rational arithmetic. □

Proposition 6.5 (Off-chain leakage). [D] *Under H_{reg} the probability that a unit leaves $\mathcal{P}$ before export is at most $\epsilon_{\mathrm{off}}\,\mathbb{E}[\#\textit{substitution steps}] \le 4\epsilon_{\mathrm{off}}$.*

Proof. Add to each state $n \le 3$ an absorbing off-chain exit of rate ω_n. The probability of using it from n, given a visit, is $\omega_n/(\lambda_n + \omega_n) \le \epsilon_{\mathrm{off}} k_{n+1}/\lambda_n$. Summing over the visits, the off-chain probability is at most $\epsilon_{\mathrm{off}} \sum_n \mathbb{P}(\text{reach } n)\, k_{n+1}/\lambda_n = \epsilon_{\mathrm{off}}\mathbb{E}[\#\text{steps}]$, the reach probabilities being those of the chain without the off-chain exits, which dominate. There are at most four steps. □

Remark 6.6. [A] The bound is conservative: an off-chain set such as $\{3, 6\}$ may itself be completed to T, so leaving $\mathcal{P}$ is not necessarily loss.

Theorem 6.7 (Axis-selectivity window). [D] *Fix $q > 1$ and $\epsilon_1, \epsilon_3 \in (0, 1)$. Under H_{trans} there is an export scale e_0 with $\mathbb{P}(\textit{exit at } 1 \mid \textit{reach } 1) \le \epsilon_1$ and $\mathbb{P}(\textit{advance past } 2 \mid \textit{reach } 2) \le \epsilon_3$ if and only if $k_2/k_3 \ge (1 - \epsilon_1)(1 - \epsilon_3)/(q\,\epsilon_1\epsilon_3)$.*

Proof. The conditions read $e_1 \le k_2\epsilon_1/(1 - \epsilon_1)$ and $qe_1 = e_2 \ge k_3(1 - \epsilon_3)/\epsilon_3$. An e_1 satisfying both exists iff the lower bound does not exceed the upper. □

Remark 6.8. [A] The per-arm enhancement widens the window: the disubstituted unit leaves q times faster than the monosubstituted one. At $\epsilon_1 = \epsilon_3 = 0.1$, $q = 10$, the threshold is $k_2/k_3 \ge 8.10$ (V2). The filing's simultaneous 6,12-bromination followed by the 3-position (clause (i)) is the documented form of this window, and under the adopted kinetics it is met with a wide margin.

Proposition 6.9 (Completion identity; the bottleneck). [D] *$p_4/p_3 = k_4/e_3$ ([A]). Under H_{trans} and the window conditions, $p_4/p_3 \le (k_4/k_3)\,\epsilon_3/(q(1-\epsilon_3))$, so $p_4 \ge p_3$ requires $k_4/k_3 \ge q(1 - \epsilon_3)/\epsilon_3$.*

Proof. By Theorem 6.4, $p_4/p_3 = (k_4/\lambda_3)(e_4/\lambda_4)/(e_3/\lambda_3) = k_4/e_3$, since $\lambda_4 = e_4$. With $e_3 = qe_2$ and $e_2 \ge k_3(1 - \epsilon_3)/\epsilon_3$ the bound follows. □

Scholium 6.10 (Slow completion is the regime to avoid). If the fourth step is no faster than the third, the trisubstituted unit leaves before it is completed. With $(k_1, k_2, k_3, k_4) = (2, 1, 0.002, 0.001)$ and $q = 10$ (V2), $p_2 = 0.903$ but $p_4 = 1.81 \times 10^{-7}$ ($p_4/p_3 = 1.0 \times 10^{-4}$), and the source must process $\Phi = 1.2 \times 10^9$ units per period at efficiency 3.7×10^{-5} (V5). The tetrasubstituted output would bind the throughput. The adopted kinetics avoid this regime by making the fourth step prompt.

7 The adopted kinetics and the matched source

Hypothesis 7.1 (H_{kin}, the author's kinetics). [D]

(K1) A (clause (i)): the 6- and 12-substitutions are nearly simultaneous, $k_1, k_2 \gg e_0, e_1$.

(K2) S: the third substitution takes time, $k_3 \ll e_2$.

(K3) S, adopted as a stated *design requirement* rather than a chemical expectation: the fourth follows after a short delay, $k_4 \gtrsim e_3$, quantified by Proposition 7.5. The statistical factors of Lemma 4.2 favour the third step, so (K3) demands positive cooperativity across the ring system, for which no electronic mechanism is offered here. It is the paper's least supported premise, and the headline efficiency depends on it.

(K4) S: the tetrasubstituted unit is removed most quickly, by its enhanced solubility, so $e_4 = qe_3$ is the largest export rate.

Theorem 7.2 (Design equation). [A] $\dfrac{p_2}{p_4} = \dfrac{e_2}{k_3}\left(1 + \dfrac{e_3}{k_4}\right)$. *Hence the exported D:T ratio equals a prescribed R_D/R_T if and only if*

$$k_3 = e_2\,\frac{R_T}{R_D}\left(1 + \frac{e_3}{k_4}\right).$$

Proof. By Theorem 6.4, with the common factor $A = \prod_{j<2} k_{j+1}/\lambda_j$,

$$p_2 = \frac{Ae_2}{\lambda_2}, \qquad p_4 = A\,\frac{k_3}{\lambda_2}\,\frac{k_4}{\lambda_3}\,\frac{e_4}{\lambda_4} = \frac{A\,k_3k_4}{\lambda_2\lambda_3}.$$

Divide, with $\lambda_3 = e_3 + k_4$. □

Theorem 7.3 (Efficiency of the matched source). [A] *Suppose the design equation holds and the initiator demand satisfies $R_I \le \Phi_{\min}p_3$. Then the material efficiency $\eta = (R_D + R_I + R_T)/\Phi_{\min}$ of Theorem 10.3 satisfies*

$$\eta \;\ge\; \eta_{DT} := \frac{R_D + R_T}{\Phi_{\min}} \;\ge\; 1 - \frac{e_0}{k_1} - \frac{e_1}{k_2} - \frac{R_T}{R_D + R_T}\cdot\frac{e_3}{k_4}.$$

Proof. Matching gives $\Phi_{\min} = R_D/p_2 = R_T/p_4$, and $R_I \le \Phi_{\min} p_3$ keeps R_I/p_3 from binding. So $\eta \ge (R_D+R_T)/\Phi_{\min} = p_2 + p_4 = 1 - p_0 - p_1 - p_3$. Now $p_0 = e_0/(e_0+k_1) \le e_0/k_1$; $p_1 \le e_1/(e_1+k_2) \le e_1/k_2$; and by Proposition 6.9, $p_3 = p_4 e_3/k_4$ with $p_4 = (p_2+p_4)R_T/(R_D+R_T) \le R_T/(R_D+R_T)$. □

Corollary 7.4 (The matched source, illustrated)**.** D *With $q = 10$, $e_n = 0.01\,q^n$, $k_1 = k_2 = k_4 = 100$ (all in units of $e_2 = 1$), demand $R_D = 42{,}354$, $R_T = 208$ and $R_I = c_I = 1$ (Definition 10.1), and $k_3 = 5.40 \times 10^{-3}$ from the design equation: $p_2 = 0.994$, $p_4 = 4.88\times10^{-3}$, $p_3 = 4.88\times10^{-4}$, $p_1 = 9.99\times10^{-4}$, $p_0 = 1.00\times10^{-4}$; $\Phi_{\min} = 42{,}630$ per period. The source makes $\Phi_{\min} p_3 = 20.8$ initiator units per period, so the hypothesis $R_I \le \Phi_{\min} p_3$ of Theorem 7.3 holds; $\eta_{DT} = 0.998413$ against the bound 0.998411, and $\eta = 0.998437$ (V1).*

Proof. Theorems 6.4, 7.2, 7.3, evaluated exactly in V1, which asserts both $p_2/p_4 = R_D/R_T$ and $c_I \le \Phi_{\min} p_3$. □

Proposition 7.5 (The cooperativity trade-off)**.** D *Under H_{trans} and the design equation, writing $x = e_3/k_4$,*

$$\frac{k_4}{k_3} = \frac{q\,\rho^*}{x\,(1+x)}.$$

At $q = 10$ and the ρ^* of Corollary 7.4, k_4/k_3 is 18,511, 1,018 and 18.5 at $x = 0.1$, 1 and 10, with exact initiator fractions $p_3 = 0.05\%$, 0.49% and 4.65% after re-matching (V1). The per-site ratio θ'_x/θ_x of Lemma 4.2 is twice k_4/k_3.

Proof. The design equation gives $e_2/k_3 = \rho^*/(1+x)$, and $k_4 = e_3/x = q\,e_2/x$ by H_{trans}; divide. V1 asserts the identity exactly at each x and recomputes p_3 from Theorem 6.4. □

Remark 7.6 (What "a short delay" must mean)**.** A Three terms enter the efficiency bound: e_0/k_1, e_1/k_2 and the initiator term $\frac{R_T}{R_D+R_T}\,e_3/k_4$, which is at most 0.05%, 0.49% and 4.89% of throughput at $e_3/k_4 = 0.1$, 1 and 10; the exact re-matched losses are in Proposition 7.5. The delay from I to T must be short compared with I's own export time and need not be very short. What the choice costs is cooperativity: tolerating a few per cent of surplus initiator lowers the required k_4/k_3 from about a thousand to under twenty. The illustration's $k_4/k_3 = 18{,}511$ is the $x = 0.1$ end of that trade-off, forced by matching rather than by efficiency.

Remark 7.7 (The exit rate of the tetrasubstituted unit)**.** A e_4 does not appear in (p_n): in the first-order chain a T unit has nowhere to go but out, so its exit rate fixes only its residence time $1/e_4$ in β and enters the decay rate of Theorem 9.4. The author's reading of (K4)—that rapid removal of T leaves more time for I to convert—is carried here by (K3), $k_4 \gtrsim e_3$. In a capacity-limited bulk, where resident T competes with I for reagent or for export sites, e_4 would enter the composition directly; that variant is Target 14.4.

7.1 The two-zone variant (not adopted)

Remark 7.8. A If the x-axis steps occurred in σ instead of β, the conversion $D \xrightarrow{a} I \xrightarrow{b} T$ would run without export competition for a residence time t, with the Bateman solution $D = e^{-at}$, $I = \frac{a}{b-a}(e^{-at} - e^{-bt})$, $T = 1 - D - I$ [Bat10]. That variant is excluded by H_{loc}; the next proposition records what it would require.

Proposition 7.9 (Low-conversion crossing)**.** A *Let $r = b/a \ge 2$ and $\delta(r) = 1 - D(t_\times)$, where $t_\times$ is the first $t > 0$ with $T(t) = I(t)$. Then $r\,\delta(r) \to x^*$ as $r \to \infty$, $x^* = 1.5936$ being the positive root of $x = 2(1 - e^{-x})$, with $|r\delta(r) - x^*| = O(1/r)$.*

Proof. Put $s = bt$, so $at = s/r$, and $G_r(s) := r\,(T - I) = r(1 - e^{-s/r}) - \frac{2r}{r-1}(e^{-s/r} - e^{-s})$. Let $G(s) = s - 2(1 - e^{-s})$. On $[0,3]$, $|r(1-e^{-s/r}) - s| \le s^2/(2r)$ and $|\frac{2r}{r-1}(e^{-s/r} - e^{-s}) - 2(1-e^{-s})| \le (2s+2)/(r-1)$, so $\sup_{[0,3]} |G_r - G| \le 13/(r-1)$. Next, $G_r'(0) = 1 - 2 = -1$ exactly, and $|G_r''| \le 6$ on $[0,3]$ for $r \ge 2$, so $G_r(s) \le -s + 3s^2 < 0$ on $(0, \frac{1}{3})$. G is convex ($G'' = 2e^{-s} > 0$) with $G(0) = 0$, $G'(0) = -1$, so its only positive zero is x^*, $G < 0$ on $(0, x^*)$, and $G'(x^*) = 1 - 2e^{-x^*} = x^* - 1 > 0$, using $e^{-x^*} = 1 - x^*/2$. For large r, uniform convergence keeps $G_r < 0$ on $[\frac{1}{3}, x^* - \upsilon]$ for each fixed $\upsilon > 0$. The same estimates applied to derivatives give $G_r' \to G'$ uniformly on $[0,3]$ at rate $O(1/r)$, so for large r, $G_r' \ge (x^* - 1)/2$ on a fixed neighbourhood of x^*, which gives a unique zero s_r with $|s_r - x^*| \le 2 \sup |G_r - G|/(x^* - 1) = O(1/r)$. Finally $\delta(r) = 1 - e^{-s_r/r} = s_r/r + O(r^{-2})$, so $r\delta(r) = s_r + O(1/r)$. □

Remark 7.10. A V3 gives $\delta = 0.00159$ at $r = 1000$ and $r\delta - x^* \approx 1.8/r$, consistent with the $O(1/r)$ rate. A stopped sequential chain overproduces its intermediate unless the last step is fast; the adopted single-zone kinetics meet the same requirement through (K3).

8 The stock phase: columns and buffering

Definition 8.1 (Two-species stacking)**.** D In κ a column of length ℓ is a word $w \in \{A, B\}^{\ell}$ (A admitted stock, B impurity) of statistical weight $W(w) = \prod_i c_{w_i} \prod_i K_{w_i w_{i+1}}$, with free monomer activities c_A, c_B and symmetric stacking constants $K_{AA} = K$, $K_{AB} = K_{BA} = K'$, $K_{BB} = K''$ [Mar96].

Hypothesis 8.2 (H_{stack})**.** D S. The admitted degrees stack with a common constant, $K_{DD} = K_{DT} = K_{TT} = K$, so that D and T count as one species A. Without it the minority T would itself be excluded from columns by the factor $(K_{DT}/K_{DD})^2$ of Theorem 8.3, which would penalise exactly the stream the protocell needs.

Theorem 8.3 (Column impurity)**.** A *Assume $K' > 0$. Let $M_{xy} = K_{xy} c_y$ and $S = \mathrm{diag}(c)^{1/2} K \,\mathrm{diag}(c)^{1/2}$. As $\ell \to \infty$ the weighted fraction of B sites in columns of length ℓ converges to $\pi_B = v_B^2/(v_A^2 + v_B^2)$, v the Perron eigenvector of S, with error $O(1/\ell)$. If moreover $Kc_A > K''c_B$,*

$$\pi_B \;\le\; \left(\frac{K'}{K}\right)^2 \frac{c_B}{c_A}\left(1 - \frac{K''c_B}{Kc_A}\right)^{-2}.$$

Proof. $W(w) = c_{w_1} \prod_i M_{w_i w_{i+1}}$, a weighted path of the transfer matrix M. $S = D^{1/2} M D^{-1/2}$ with $D = \mathrm{diag}(c)$ is symmetric and nonnegative; with $K' > 0$ it is irreducible and, having positive off-diagonal entries on two states, primitive. If $Sv = \lambda v$ for its Perron root λ, then $\psi = D^{-1/2} v$ and $\phi = D^{1/2} v$ are the right and left Perron vectors of M, and $\phi_x \psi_x = v_x^2$. The Doob transform $P_{xy} = M_{xy}\psi_y/(\lambda \psi_x)$ is a primitive stochastic matrix with stationary law $\phi_x \psi_x$ [Sen81]. The column weight differs from the P-path measure by the factor $c_{w_1} \lambda^{\ell - 1}/(\phi_{w_1} \psi_{w_\ell})$, which depends only on the two end letters and is bounded above and below. Interior sites at distance j from both ends have marginal law within $O(\rho^{\,j})$ of $\phi_x \psi_x$, where $\rho < 1$ is the second eigenvalue modulus of P; summing over sites, the $O(1)$ sites near the ends contribute the $O(1/\ell)$ error. For the bound, $\lambda \ge Kc_A$ (Rayleigh quotient at e_A), and the second row of $Sv = \lambda v$ with $v = (1, t)$ gives $t = K'\sqrt{c_A c_B}/(\lambda - K''c_B)$, which is positive and at most $K'\sqrt{c_A c_B}/(Kc_A - K''c_B)$. Then $\pi_B = t^2/(1 + t^2) \le t^2$. □

Remark 8.4 (Why the square)**.** A An impurity inside a column replaces two A–A contacts by two A–B contacts, so its weight relative to an A is $(K'/K)^2 c_B/c_A$; only the two ends pay a single factor, which is the $O(1/\ell)$ error. In V8 ($K = 1$, $K' = 0.2$, $K'' = 0.1$, $c_A = 0.9$, $c_B = 0.01$) the Perron limit is 4.448×10^{-4} against the bound 4.454×10^{-4}, the exact length-200 value is 4.63×10^{-4}, its Richardson extrapolation is 4.448×10^{-4}, and the first-power estimate $K' c_B/(Kc_A) = 2.22 \times 10^{-3}$ is about five times too large.

Hypothesis 8.5 (H_{rgy}, arm registry)**.** D S. In a column of armed chrysene the units stack face to face along z at the spacing of $\|T_z\|$, and the C_{2h} symmetry of the core places the arms of one unit over the arms of the next, so that a tetrasubstituted stack carries four continuous columns of arms and a disubstituted stack two. Write ν for the number of arm registrations a single stacking contact carries, so $\nu = 4$ for T and $\nu = 2$ for D, and $\Delta_{\mathrm{rgy}} > 0$, in units of $k_B T$, for the free energy of one registration. A guest that does not present the pattern breaks every registration at both of its contacts, so that

$$\frac{K'}{K} \;=\; e^{-\Delta_\pi}\, e^{-\nu \Delta_{\mathrm{rgy}}},$$

with Δ_π the π-mismatch alone. By Corollary 4.5 no four-ring competitor presents the pattern; a competitor of another ring count is not covered.

Corollary 8.6 (Registry suppresses the column impurity exponentially)**.** D *Under H_{rgy} and the hypotheses of Theorem 8.3,*

$$\pi_B \;\le\; e^{-2\nu\Delta_{\mathrm{rgy}}}\, e^{-2\Delta_\pi}\, \frac{c_B}{c_A}\left(1 - \frac{K''c_B}{Kc_A}\right)^{-2}.$$

The suppression relative to the π-mismatch alone is $e^{-2\nu\Delta_{\mathrm{rgy}}}$: at $\Delta_{\mathrm{rgy}} = 1$ it is 0.0183 for $\nu = 2$ and 3.35×10^{-4} for $\nu = 4$, and at $\Delta_{\mathrm{rgy}} = 2$ it is 3.35×10^{-4} and 1.13×10^{-7}. Applied to the sample composition of V8 the bound falls from 4.454×10^{-4} to 8.16×10^{-6} and 1.49×10^{-7} at $\Delta_{\mathrm{rgy}} = 1$, and to 1.49×10^{-7} and 5.01×10^{-11} at $\Delta_{\mathrm{rgy}} = 2$ (V13).

Proof. Substitute the factorisation of H_{rgy} into the bound of Theorem 8.3, which carries $(K'/K)^2$ because an interior guest pays two contacts. □

Scholium 8.7 (The monograph's corona, quantified). This is the monograph's own physical reading in a form that carries a number. Chapter 2 argues that an errant molecule "fails to interleave its hydrophilic substituents" with the lattice, breaking a continuous hydrophilic corona and exposing hydrophobic surface to the solvent [Sch26f, §2.3.3]. That is the registry deficit. Where the monograph sent the resulting penalty to a threshold and then to an infinite metric, here it is a free energy per registration and enters as an exponential factor, which is

finite, falsifiable and small rather than infinite.

Theorem 8.8 (Buffering). [A] *For one species with isodesmic constant K, total concentration c and free monomer concentration c_1, $c = c_1/(1-Kc_1)^2$ for $Kc_1 < 1$, so that*

$$Kc_1 = \frac{2Kc + 1 - \sqrt{4Kc+1}}{2Kc} < 1,$$
$$Kc_1 \to 1 \ \ (c \to \infty), \qquad Kc_1 \geq \tfrac{1}{2} \ \text{ when } Kc \geq 2.$$

Proof. $c = \sum_{j\geq 1} jK^{j-1}c_1^j = c_1(1-Kc_1)^{-2}$. With $x = Kc_1$, $y = Kc$: $y(1-x)^2 = x$, whose root in $(0,1)$ is displayed; it increases in y and equals $\frac{1}{2}$ at $y = 2$. □

Remark 8.9. [A] The isodesmic model buffers asymptotically and has no sharp critical concentration. A cooperative (nucleation–elongation) model would give one; nothing below needs it.

Hypothesis 8.10 (H_{leq}). [D] An impurity $d \in \mathcal{D}$, which is not substituted, is in partition equilibrium between β and the free monomer pool of σ: $c_d^\sigma = P_d c_d^\beta$.

Proposition 8.11 (Selectivity at the column, however the competitor arrived). [D] *Assume H_{stack}, H_{rgy} and $K' > 0$, and assume of the* free *stock monomer that $Kc_A \geq \frac{1}{2}$ and $Kc_A > K''c_d^\sigma$. Then for every $d \in \mathcal{D}$ present in the stock phase at free concentration c_d^σ, armed or not, the impurity fraction of κ satisfies*

$$\pi_d \ \leq \ 2K\, e^{-2\Delta_\pi}\, e^{-2\nu\Delta_{\text{rgy}}}\, c_d^\sigma \left(1 - \frac{K''c_d^\sigma}{Kc_A}\right)^{-2}.$$

If moreover H_{leq} and H_{bulk} hold, then $c_d^\sigma = P_d c_d^\beta \leq P_0 c_d^\beta$ and the bound may be written in bulk quantities.

Proof. Theorem 8.3 and Corollary 8.6 with $c_B = c_d^\sigma$, together with $c_B/c_A \leq 2Kc_B$ from $c_A \geq 1/(2K)$. The second sentence substitutes H_{leq} and H_{bulk}. □

Remark 8.12 (What the restatement costs and buys). [A] The bound is linear in c_d^σ and carries the registry factor whatever that concentration is. So a failure of H_{sel}—competitors armed, and partitioning into σ along with the stock—raises the bound in proportion to how much of the bulk is armed, and no further. It does not reopen the question of whether the columns can be kept clean, which is settled by $e^{-2\nu\Delta_{\text{rgy}}}$ and by the geometry that Corollary 4.5 denies to a four-ring competitor.

Remark 8.13. [A] The free-monomer assumption is made directly rather than deduced from Theorem 8.8: that theorem is for one species, and in a two-species column the impurity co-stacks and sequesters further A, so $Kc_{\text{total}} \geq 2$ does not imply $Kc_A \geq \frac{1}{2}$.

Scholium 8.14 (Four filters, and what each is worth). Selectivity against the background is not one mechanism but four, acting at different places on different properties. They are listed in the order a molecule meets them, with the paper's standing in each.

(1) *Arming, in the bulk.* The bromination is regioselective on chrysene, the 6- and 12-positions first and together, which the filing's experiment attests (clause (i)). Whether the same reagent leaves the rest of the bulk alone is H_{sel}, which is stated and not shown—and which, by the restatement of Proposition 8.11, no result needs. A failure here raises c_d^σ and nothing else.

(2) *Partition, from bulk to stock.* Export rises as q^n in the number of arms. This stage does *not* discriminate an armed competitor at degree two from D: both carry two arms, and an armed competitor has as much reason to leave the bulk as an armed chrysene. It discriminates only at degree four, where Corollary 4.5 denies the pattern to any four-ring competitor.

(3) *Admission, at export.* A core that is not a chrysene in one of Article 77's three families is not admitted, whatever arms it carries (Theorem 10.7). This filter is structural and exact, but it is a predicate and not a force: it determines what counts as stock, not what is physically present in σ.

(4) *Registry, at the column.* A guest that cannot present the pattern breaks ν arm registrations at each of two contacts, so its incorporation carries $e^{-2\nu\Delta_{\text{rgy}}}$ (Corollary 8.6). This is the filter that acts physically on an armed competitor already in the stock phase, and it is the only one that protects the disubstituted stream, at $\nu = 2$ rather than 4—the factor 0.0183 between the two streams at $\Delta_{\text{rgy}} = 1$.

The structure of the argument is that (1) and (2) set how much competitor reaches the stock phase, while (3) and (4) decide what becomes of it there. Only (1) has an experimental anchor; only (3) is exact; and (4) carries the weight for the stream that is nine-tenths of the demand. The honest reading is that the separation does not depend on the arming step being selective, and does depend on Δ_{rgy} being positive and not small.

Scholium 8.15. Column purity is the product of a stacking factor $(K'/K)^2$ and the impurity's own solubility in the stock phase measured against the buffered stock monomer. Neither factor is zero, and no term in it is a symmetry.

9 Scission in this realisation

Definition 9.1 (Structural states and admissibility). D Let $X = \{0,\dots,4\} \times \{\beta,\sigma,\kappa\}$. Transitions: $(n,\beta) \to (n{+}1,\beta)$ at k_{n+1}; $(n,\beta) \to (n,\sigma)$ at e_n; $(n,\sigma) \leftrightarrow (n,\kappa)$ at $a_n, d_n > 0$; and, for $n \geq 1$, no return, by H_{ret} (the degree-0 return changes nothing below and is set to zero for brevity); and, in the open source, delivery from (n,σ) and (n,κ) at $u_n > 0$ for $n \geq 2$ only, since units of lower degree are not admitted. With the undirected skeleton $\mathcal{E}_0$ of these transitions, unit weights $w \equiv 1$ (any positive symmetric weights serve) and the constraint functional $C_1(n,\phi) = \mathbf{1}[\phi = \beta] + \mathbf{1}[n < 2]$ with $\tau_1 = 1$, this supplies items 2–4 of Axiom A12 [Sch26c]. The injective spectral realisation $\jmath_{\mathrm{str}}$ of its item 1 (eq. (413) there) is not supplied, so the instance is *partial*. Write $\Omega_{\mathrm{adm}} = \{2,3,4\} \times \{\sigma,\kappa\}$ with indicator Q_{adm}, and $Q_{\mathrm{rej}} = I - Q_{\mathrm{adm}}$ [Sch26c, eq. (434)], which is the sum of the bulk indicator Q_β and the indicator $Q_{\mathcal{W}}$ of the waste class $\mathcal{W} = \{0,1\} \times \{\sigma,\kappa\}$.

Proposition 9.2 (The infinite distance is bookkeeping). A *For $x \in \Omega_{\mathrm{adm}}$ and $y \notin \Omega_{\mathrm{adm}}$, $d^*_{\mathfrak{C}}(x,y) = +\infty$.*

Proof. Admissible paths lie in Ω_{adm} by definition [Sch26c, eq. (423)]. Under H_{ret} and H_{cov} no edge of $\mathcal{E}_0$ changes the degree in any case, so the two classes are not joined at any threshold. □

Scholium 9.3. This is all that the monograph's Theorem 2.2 established, and by Article 40 it establishes no removal. The removal is the next theorem, and what makes it a separation rather than a general decay is that the admissible weight does *not* vanish with the rest.

Theorem 9.4 (Dynamical scission). D *Assume H_{cov}, H_{loc} and H_{ret}, and take the closed source ($u_n = 0$). Let ρ be the law started at $(0,\beta)$. Then*

(a) the bulk empties: $\|\rho\, e^{t\mathcal{L}} Q_\beta\|_1 \leq C(1+t)^4 e^{-\lambda_* t}$ *with* $\lambda_* = \min_n \lambda_n$, *equal to* 1.005 *at the* V1 *rates;*

(b) Ω_{adm} and $\mathcal{W}$ are each closed: *no transition leaves either;*

(c) the two retain fixed, disjoint weights: $\rho\, e^{t\mathcal{L}} Q_{\mathrm{adm}}\mathbf{1} \uparrow p_2 + p_3 + p_4 = 0.998901$ *and* $\rho\, e^{t\mathcal{L}} Q_{\mathcal{W}}\mathbf{1} \uparrow p_0 + p_1 = 1.10 \times 10^{-3}$.

The waste weight accumulates inside *the stock phase, so the monosubstituted units it holds are themselves an impurity source for the columns, to be counted in the c_B of Theorem 8.3 unless a separate channel removes them (Target 14.10).*

Proof. (a) By H_{ret} the bulk states form an invariant block, which is the generator of Definition 6.2; Lemma 6.3 gives spectral abscissa $-\lambda_*$, and the Jordan bound for a 5×5 matrix gives the estimate with $m \leq 4$. (b) By H_{ret} the only transitions out of (n,σ) or (n,κ) are $\sigma \leftrightarrow \kappa$ at the same degree, and H_{loc} forbids substitution there; so the degree of a unit outside β never changes and neither class is left. (c) Weight enters $\{n\} \times \{\sigma,\kappa\}$ only by export at degree n, whose total probability is p_n by Theorem 6.4, and by (b) never leaves; the limits are therefore the stated partial sums, approached monotonically. □

Corollary 9.5 (Open source). D *With delivery at $u_n > 0$ from Ω_{adm}, let $G_\dagger$ be the generator restricted to $\{\beta\} \cup \Omega_{\mathrm{adm}}$ and $-\mu$ its spectral abscissa. Then $-G_\dagger$ is a nonsingular M-matrix, $\mu > 0$, and that block's weight is $O\big((1{+}t)^m e^{-\mu t}\big)$; $\mathcal{W}$ remains closed with limiting weight $p_0 + p_1$; and the delivered weight tends to $p_2 + p_3 + p_4$.*

Proof. $G_\dagger$ is Metzler with nonpositive row sums, and from every state of the block either delivery or $\mathcal{W}$ is reachable, so every such state is transient and $\rho e^{tG_\dagger} \to 0$. Were the spectral abscissa nonnegative, Perron–Frobenius for Metzler matrices, applied to $G_\dagger^{\mathsf{T}}$ and legitimate for a reducible matrix, would give a nonnegative left eigenvector whose weight does not vanish, a contradiction; hence $-G_\dagger$ is a nonsingular M-matrix [BP94], and the Jordan bound gives the stated decay. V12 certifies the M-matrix property at sample rates by an exact positive solution of $(-G_\dagger)\tau = \mathbf{1}$, the vector of mean times to leave the block (maximum 101). □

Remark 9.6 (Against Article 40, Theorem 49). D Article 40 asks that a rejected component be "removed, absorbed, or dynamically isolated" [Sch26c, Thm. 49]. Here $Q_{\mathrm{rej}} = Q_\beta + Q_{\mathcal{W}}$: the bulk part is removed, at the rate of Theorem 9.4(a), and the waste part is dynamically isolated, by (b). The statement is not vacuous because the admissible weight is retained at 0.998901 rather than decaying with it. For the diagonal (classical) states used here the coherence condition of eq. (569) holds at every t and adds nothing. The target is therefore discharged for this realisation, in the classical sector, for a *partial* instance of A12, and conditional on H_{cov} and the stipulation H_{ret}. The quantum statement is not addressed.

9.1 What the no-return premise buys

Proposition 9.7 (Returns drive the stock to full substitution). D *Suppose instead that $r_n > 0$ for every n, with $u_n = 0$, $a_n, d_n, e_n > 0$ and $k_{n+1} > 0$ for $n \leq 3$. Then the unique closed class is $\{4\} \times \{\beta,\sigma,\kappa\}$, every unit is eventually*

tetrasubstituted, and the bulk weight tends to

$$\pi(4,\beta) = \Big(1 + \frac{e_4}{r_4}\Big(1 + \frac{a_4}{d_4}\Big)\Big)^{-1} > 0,$$

which is 9.9×10^{-8} *at the sample rates of* V12*. A returned admitted unit would also be armed again in* β*, which Article 77's carbon boundary forbids.*

Proof. A state of degree $n < 4$ reaches (n,β), directly or through r_n or d_n then r_n, and thence $(n{+}1,\beta)$; by H_{cov} degree n is never revisited, so every such state is transient. The three states of degree 4 communicate and admit no exit, so they form the unique closed class; restricted to it the chain is birth–death and so reversible, giving $\pi(4,\sigma)/\pi(4,\beta) = e_4/r_4$ and $\pi(4,\kappa)/\pi(4,\sigma) = a_4/d_4$. Normalise. Convergence is exponential for a finite chain with a single closed class. □

Proposition 9.8 (Residence at fixed degree)**.** [A] *With* $r_n > 0$ *and no delivery, the mean time to return to* β *is* $(1 + a_n/d_n)/r_n$ *from* (n,σ) *and* $1/d_n + (1 + a_n/d_n)/r_n$ *from* (n,κ).

Proof. With T_σ, T_κ the mean hitting times of β: $T_\sigma = \frac{1}{r_n+a_n} + \frac{a_n}{r_n+a_n}T_\kappa$ and $T_\kappa = 1/d_n + T_\sigma$; substituting gives $T_\sigma\, r_n/(r_n + a_n) = (1{+}a_n/d_n)/(r_n{+}a_n)$. V11 checks this by an exact linear solve (amplification $1 + a/d = 101$ at the sample rates). □

Remark 9.9. [A] Propositions 9.7 and 9.8 say what H_{ret} buys: the D-rich composition is stable because admitted units do not return. Were they to return, a unit would re-enter β after a mean of 101,000 time units at the sample rates, the columns lengthening that by the factor $1 + a_n/d_n = 101$, and the stock would reach full substitution after a mean of 1.87×10^7. Read through Eyring–Kramers, the return rate is $r_n \asymp e^{-\Gamma_n/k_BT}$ with Γ_n the transfer barrier [BdH15]; H_{ret} is the statement that this barrier is large on the horizon of a period. Nothing above depends on that reading.

Remark 9.10 (Gradient-flow structure, corrected)**.** [C] A reversible exchange at fixed degree is the gradient flow of relative entropy in Maas's discrete transport metric [Maa11, EM12]. The source, driven by irreversible substitution and by absorbing export, is not the gradient flow of any free energy (Ruling 13.3).

10 The supply interface

10.1 Demand

Definition 10.1 (Demand vector)**.** [C] Per period,

$$R_D = 5L + \tfrac{\alpha}{1-\alpha}N + \nu L + 2\ell_{\mathrm{ICL}},$$
$$R_T = L + n_{\mathrm{ICL}}, \qquad R_I = c_I,$$

where the first three terms of R_D are Article 65's [Sch26d, Thm. 8.5]; $\ell_{\mathrm{ICL}} = 77$ is the bilayer-lipid demand of the minimal ICL [Sch26g, Prop. 9.1], at two disubstituted units per route-A lipid [Sch26e, Prop. 10.2]; R_T takes one tetrasubstituted unit per nucleotide pair transformed (S) and assigns Article 78's $n_{\mathrm{ICL}} = 8n_A + 8(n_{B,1} + n_{B,2}) + 16n_C$ chrysene units [Sch26g, eq. (1)] to the tetrasubstituted demand (S, H_{acc}); and $c_I = 1$ initiator per strand per period, the initiator being consumed at polymerisation, where Article 65's edge π reads $Nt + I \to St$ with I incorporated [Sch26d, block V2]. The nine pore units of [Sch26a, Prop. 3.12] are drawn once per founder (S) and belong to the founder inventory, not to the per-period demand.

Remark 10.2 (The numbers)**.** [A] At $L = 200$, $\nu = 66$, $N = 2.52 \times 10^5$, Article 65's three terms give 42,200 ($\alpha = 0.10$) and 19,343 ($\alpha = 0.02$), reproducing its block V4; with the ICL lipids, R_D = 42,354 and 19,497 (V4). With $n_A = 1$, $R_T = 208$, and $\rho^* = R_D/R_T$ is 204 and 94: the protocell draws one to two hundred disubstituted units per tetrasubstituted one. Article 62's $\nu \approx 66$ rests on a stipulated bending tolerance and moves between 22 and 219 over its swept range [Sch26e, Cor. 10.6]; every quantity here is linear in the term νL.

10.2 Throughput and efficiency

Theorem 10.3 (Supply in expectation)**.** [A] *Let the source process* Φ *bulk chrysene units per period with exit distribution* (p_n)*. The expected outputs* Φp_n *meet the demand iff* $\Phi \geq \Phi_{\min} := \max_{n:R_n>0} R_n/p_n$*, and then* $\eta = (R_D + R_I + R_T)/\Phi_{\min} \leq \sum_{n\geq 2} p_n$*, with equality iff* $p_n \propto R_n$ *on* $n \geq 2$.

Proof. $\Phi p_n \geq R_n$ for each n iff $\Phi \geq R_n/p_n$ for each n. Then $\Phi_{\min} p_n \geq R_n$ for all n, and summing over $n \geq 2$ gives $\Phi_{\min} \sum_{n\geq 2} p_n \geq \sum R_n$, with equality iff each inequality is tight. □

Remark 10.4 (The fluid limit, and fluctuations). [A] The theorem is a statement about expected outputs. The realised output at degree n is a sum of Φ independent indicators, so at $\Phi = \Phi_{\min}$ the tetrasubstituted output is approximately Poisson with mean R_T and falls short in about half of all periods; a margin of $z\sqrt{R_T}$ units above R_T reduces the shortfall probability to the Gaussian tail at z. Theorem 7.2's ratio and Proposition 10.17 are to be read the same way.

Remark 10.5. [A] Theorem 7.3 is the matched case: there $R_I \le \Phi_{\min} p_3$, so the initiator is made in surplus and the bound is approached to within p_3.

10.3 Arms and admission

Remark 10.6 (Article 77 admits by family). [C] Article 77 admits "adequate quantities of the 6,12, 3,6,12, and 3,6,9,12 families" [Sch26a, §3]; it requires of each stock type a complete constitutional specification [Sch26a, Def. 3.1]; and it allows longer arms "only as specified finite graphs" [Sch26a, §3.1]—a condition on how an arm is declared, not a list of which arms are permitted. Its Table 2 is captioned "a concrete admitted stock catalogue", and its $T0$ and Dm entries are "explicit catalogue choices within the stipulated substitution families" [Sch26a, §3.1]. Admission is therefore by family and specification, not by a list of arm words. Each of h, o, e, e_P is a specified finite arm graph, so every unit this source exports at degree ≥ 2 is admissible under Article 77 as it stands, and no widening of its predicate is proposed here.

Theorem 10.7 (Admission is independent of the arm law). [D] *Under H_{reg}, H_{seq} and Convention 2.3, for every arm law—independent or not, at any reagent purity—every unit exported at degree $n \ge 2$ along $\mathcal{P}$ is admissible under Article 77's predicate. The non-admitted fraction is at most $p_0 + p_1 + 4\epsilon_{\text{off}}$, and no arm-scheduling hypothesis is required.*

Proof. An exit at degree $2, 3, 4$ along $\mathcal{P}$ carries one of Article 77's three substitution families, with arms in $\mathcal{A}$, each a specified finite graph (Remark 10.6); by H_{seq} every substituted position carries a declared arm, so no residual bromine enlarges the locant set beyond its family; the record kept at export supplies the constitutional specification its Definition 3.1 requires (Convention 2.3). Exits at degrees 0, 1 carry no family and are refused. Off-chain exits are bounded by Proposition 6.5. □

Lemma 10.8 (Arm words within the families). [A] *Up to ι, the arm words on D, I and T number $3 + 8 + 10 = 21$ over $\{h, e\}$ and $6 + 27 + 45 = 78$ over $\{h, e, e_P\}$. Article 77's Table 2 lists five of the first twenty-one, as explicit choices within the families.*

Proof. With m arm types: on D the inversion swaps the two sites, giving $m(m+1)/2$ words; I is carried by ι to $\{6, 9, 12\} \ne I$, so each orbit has one representative on $\{3, 6, 12\}$ and there are m^3; on T the inversion acts as $(3\,9)(6\,12)$ and Burnside gives $(m^4 + m^2)/2$. V9 confirms both counts by enumeration. □

Hypothesis 10.9 (H_{acc}, acceptance sets). [D] S. Fitness of a unit for a use is an allocation constraint, settled inside Article 77's packet criterion (M3) [Sch26a, Def. 3.7, Thm. 3.8], not at admission: the transformation and the ICL accept $T2$, phosphorylated downstream to e_P as required; the initiator use accepts $I2$; anchors and residues accept $\{D2, Dm\}$; the membrane accepts $\{D2, Dm\}$, with $D2$ processed by Article 62's route A and its four-carbon complement entered as a declared coproduct.

Theorem 10.10 (No cleavage, no arm loss). [D] *Under H_{acc} and H_{arm}, if no oxalate arm is cleaved ($\pi_e = 1$) then every per-period use is met with arm efficiency 1, provided Article 77's open obligation for route-A membranes from $D2$—an explicit transformation routing the four extra arm carbons to a coproduct pool [Sch26a, Prop. 3.10, App. A.3]—is discharged.*

Proof. With $\pi_e = 1$ the only arm words produced are ee on D, eee on I and $eeee$ on T, that is $D2$, $I2$, $T2$, each lying in the acceptance set of H_{acc} for its degree. The pore's $T0$ units are a founder quantity and lie outside the per-period demand (Definition 10.1). □

Proposition 10.11 (Cleavage). [D] *If each arm is cleaved to h independently with probability $\pi_h = 1 - \pi_e$, then under H_{acc} the accepted fractions are $1 - \pi_h^2$ on D and π_e^4 on T, and after re-matching the design equation to the accepted streams the arm efficiency is*

$$\eta_{\text{arm}} = \frac{R_D + R_T}{R_D/(1 - \pi_h^2) + R_T/\pi_e^4},$$

equal to 0.9997, 0.9964 and 0.9875 at $\pi_e = 0.99, 0.95$ and 0.90 (V9). Unaccepted units remain admitted, as surplus stock available to any use that accepts them.

Proof. On D only hh is unaccepted, with probability π_h^2; on T only $eeee$ is accepted, with probability π_e^4. Re-matching the $D{:}T$ exit ratio to the accepted streams makes the two required throughputs additive. □

Remark 10.12 (Phosphate arms)**.** [E] Phosphorylating an h-arm gives an aryl phosphate monoester, the precursor of the short aryl phosphodiester linker of Article 66's pore (as cited in [Sch26a, §2.3]); phosphorylating an e-arm gives the alkyl monoester e_P and, on condensation, Article 62's long $-\mathrm{O}-\mathrm{CH_2CH_2}-\mathrm{O}-\mathrm{P}$ linker. The two differ in contour length and in lability: aryl monoesters hydrolyse faster, which is where H_{arm} is weakest. The alphabet carries no h_P because phosphorylation occurs downstream of admission.

10.4 Carbon and delivery

Proposition 10.13 (Upstream carbon ledger)**.** [D] *Let n_c count a unit's two-carbon arms (o, e or e_P), E_o the oxalate arms installed over an execution and N_{cl} the arms cleaved. Then*

$$18\,\Phi_{\mathrm{in}} + 2E_o \;=\; \sum_{\text{admitted}} (18+2n_c) \;+\; \sum_{\text{waste}} (18+2n_c) \;+\; \sum_{\text{resident}} (18+2n_c) \;+\; 2N_{\mathrm{cl}},$$

where Φ_{in} counts the chrysene cores that have entered the process, "waste" the exports of degree 0 *and* 1 *and the off-chain units, "resident" the units still in the bulk, and the last term the oxalate carbon released by cleavage. Oxalate is the only carbon-bearing reagent incorporated; bromine, the reductant and the phosphate are carbon-free, and any solvent is declared and not incorporated (H_{cat}). Unaccepted admitted units count as admitted.*

Proof. Article 77's open balance [Sch26a, Thm. 3.5, (M2)] applied upstream with export as the admission event: bromination moves no carbon, each oxalate substitution adds exactly two carbons, reduction and phosphorylation preserve them (Proposition 4.8), cleavage removes two, and every core ends in exactly one of the three classes. Resident units are credited with their installed arms, not as bare cores. □

Remark 10.14. [A] For the source of Theorem 10.10 at $\alpha = 0.10$, the carbon in the disubstituted and tetrasubstituted demand is 937,196 per period; the initiator drawn adds 24, and all the initiator made carries 499. Of the first figure, 26,708 is the four-carbon complement of the route-A lipids of the membrane and the ICL (V7). Supplying part of the membrane as Dm would avoid that complement, at the cost of cleaved arms elsewhere (Proposition 10.11).

Proposition 10.15 (Delivery: a necessary condition)**.** [D] *Under H_{phase}, let a vessel of radius R_v capture units from a medium at free stock monomer concentration c_1 (in mol m^{-3}), with diffusivity D_{m}. The Smoluchowski perfect-sink rate $4\pi D_{\mathrm{m}} R_v N_A c_1$, with N_A Avogadro's number, is an upper bound on the capture rate [vS17]. Since $c_1 < 1/K$ (Theorem 8.8), a demand of n units per period δT can be met by diffusion only if*

$$4\pi D_{\mathrm{m}} R_v N_A\, \delta T\, /K \;\geq\; n.$$

At $D_{\mathrm{m}} = 5\times10^{-10}\,m^2 s^{-1}$, $R_v = 10\,nm$ and $\delta T = 12\,h$, the concentrations required are $4.9\times10^{-15}\,M$ for the ICL demand alone and $2.6\times10^{-11}\,M$ for the whole demand, and the condition reads $K \leq 3.8\times10^{10}\,M^{-1}$ (V10).

Proof. Capture over a period is at most $4\pi D_{\mathrm{m}} R_v N_A c_1 \delta T$, and $c_1 < 1/K$. □

Remark 10.16. [A] The condition is necessary and not sufficient: the realised c_1 can lie far below $1/K$, and excluding diffusion would not by itself identify the binding step, which may be desorption from a column or transport within σ. One period's disubstituted supply occupies several times the volume of a 10 nm vessel, so a self-consistent R_v is larger; since capture scales with R_v, the ceiling on K only rises. Chromonic assembly in water is isodesmic [ZC22]; the stacking constant of this stock is Target 14.8, and whether membrane entry is the binding step, as Article 78 anticipates (its Remark 7.2 and Target 11.4), is not settled here.

Proposition 10.17 (Finite bulk)**.** [D] *Under H_{cov} and H_{ret}, a bulk holding M chrysene units supports at most $\lfloor M/\Phi_{\mathrm{min}} \rfloor$ periods of supply in expectation.*

Proof. Each period withdraws Φ_{min} units in expectation and none returns to degree 0. □

Remark 10.18. [A] This is the replenishment that Article 77's Proposition 9.3 requires and does not construct, and it is finite: the source replaces a finite reserve with a larger finite reserve. Article 65's lifetime demand of order 1.7×10^6 units per founder over forty buds [Sch26d, Thm. 8.5] bounds M from below, after division by the efficiency.

11 Consolidated register

What makes a chrysene leave the bulk? Its own arms. *Rests on* H_{add}, H_{trans}, Thm. 5.1. *Standing* D .

What installs the arms? Bromination, 6 and 12 together and then 3; oxalate substitution; reduction. *Rests on* Def. 4.7: the sequence and the oxalate arm A by clause (i), the calcium oxalate reagent and the reduction S; H_{seq}, H_{cat}, H_{sel}, H_{arm}. *Standing* D .

At which degree does a unit leave? With probability p_n, in closed form. *Rests on* Thm. 6.4. *Standing* A ; checked against the fundamental matrix.

Can the stream match the protocell's demand? Yes, by one design equation, with $\eta \geq 1 - e_0/k_1 - e_1/k_2 - \frac{R_T}{R_D+R_T} e_3/k_4$ provided $c_I \leq \Phi_{\min} p_3$, which holds at the illustration. *Rests on* Thms. 7.2, 7.3, Cor. 7.4. *Standing* A for the identities; the kinetics A/S.

What does that cost kinetically? $k_4/k_3 = q\rho^*/(x(1+x))$: about a thousand at a half per cent initiator loss, under twenty at five per cent. *Rests on* Prop. 7.5. *Standing* D ; (K3) is the least supported premise.

What happens if completion is slow? The tetrasubstituted output binds the throughput. *Rests on* Prop. 6.9. *Standing* D .

Is the stock pure? No; column impurity is bounded by a stacking square times a solubility, and the stacking factor is itself exponentially small in the arm registrations a guest breaks. *Rests on* Thm. 8.3, Cor. 8.6, Prop. 8.11; H_{sel}, H_{rgy}, H_{stack}, H_{leq}. *Standing* A /D .

What keeps the background out? Four filters: arming, partition, admission and registry. The separation does not require the first to be selective; the fourth carries the disubstituted stream. *Rests on* Scholium 8.14, Cors. 4.5, 8.6, Thm. 10.7. *Standing* C /D .

Must the arming reagent act on chrysene alone? No. An unselective reagent raises c_d^{σ}, in which the column bound is linear, and leaves the registry factor and the admission predicate untouched. *Rests on* Prop. 8.11 as restated; H_{sel} is optional. *Standing* D .

Is chrysene singled out among its neighbours? Within the four-ring polyhexes, yes, by enumeration: it is the one of seven with the reference C_{2h} group. Other ring counts are not covered. *Rests on* Prop. 4.4, Cor. 4.5. *Standing* C .

In what sense is the separation irreversible? With returns disallowed: the bulk empties exponentially, the admissible stock keeps weight 0.998901, and the low-degree exports are dynamically isolated. *Rests on* Thm. 9.4, Cor. 9.5; H_{cov}, H_{ret}. *Standing* D ; discharges Article 40's Target 49 in the classical sector, for a partial A12 instance.

What would returns do? The stock would relax to full substitution, and admitted carbon would be modified, which Article 77 forbids. *Rests on* Props. 9.7, 9.8. *Standing* D .

Does Article 77's predicate need changing? No. It admits by family and specification, and every arm here is a specified finite graph; admission is independent of the arm law, so cleaved arms cost efficiency but never admissibility. *Rests on* Rem. 10.6, Thm. 10.7, Prop. 10.11. *Standing* C /D .

Is diffusion the binding step of delivery? Not determined. Diffusion can fail to bind only if $K \leq 3.8 \times 10^{10}\,\mathrm{M}^{-1}$; the binding step is not identified. *Rests on* Prop. 10.15. *Standing* D .

12 Falsification register

H_{add}, H_{trans}. A transfer free energy that does not fall with arm count, or a return barrier that grows with it, removes the cause of export. Theorem 6.4, the design equation and the efficiency bound survive with general e_n; the window, the bottleneck and Proposition 7.5 do not.

H_{kin} (K3). $e_3/k_4 \gg 1$ moves the source into the regime of Proposition 6.9; before that the efficiency degrades linearly in e_3/k_4. A measured k_4/k_3 below the curve of Proposition 7.5 at every tolerable loss refutes the matched source.

H_{kin} (K1). A slow second y-step ($k_2 \lesssim e_1$) exports monosubstituted waste in proportion $e_1/(e_1+k_2)$; the filing's simultaneous 6,12-bromination is evidence against this failure.

H_{cov}. A reversible substitution removes the irreversibility of Theorem 9.4.

H_{ret}. Any return of admitted units invalidates Theorem 9.4(b) and brings in Proposition 9.7; it would also breach Article 77's carbon boundary.

H_{sel} (optional). Its failure raises c_d^{σ} and with it, linearly, the column bound of Proposition 8.11. It falsifies no result, because no result assumes it.

H_{rgy}. A measured K'/K that does not fall with the number of arms, or a guest incorporated at the rate the π-mismatch alone predicts, removes the registry stage. Theorem 8.3 survives with K' as a free parameter; Corollary 8.6 does not, and with it goes the only stage that protects the disubstituted stream.

H_{seq}. A reduction slower than export sends o-armed units to the stock; they remain admissible and the carbon count is unchanged.

H_{stack}. $K_{DT} \neq K_{DD}$ excludes the minority T from columns by the square of the ratio.

H_{phase}. A lamellar or purely interfacial stock phase invalidates Props. 5.3, 8.11, 10.15 and Thm. 8.8 as stated.

H_{acc}**.** A per-period use accepting only h-arms or only mixed words would change Theorem 10.10; Theorem 10.7 survives, and Proposition 10.11 gives the cost.

13 Precedence

Ruling 13.1 (Against the monograph, Ch. 2, Thm. 2.1)**.** A Superseded. Orthogonal decoupling ($\gamma = 0$) is not used. Exclusion is graded, by transfer free energy and by the square of the stacking ratio, and is never total.

Ruling 13.2 (Against Ch. 2, Thm. 2.2, Def. 2.3, Thms. 2.4–2.5)**.** A Superseded. $d^{*}_{\mathfrak{C}} = \infty$ is bookkeeping; $K^{0}(X \sqcup Y) \cong K^{0}(X) \oplus K^{0}(Y)$ holds for every disjoint union and carries no dynamical content. The content is Theorem 9.4 and Corollary 9.5. The monograph attaches its irreversibility to the precipitated conglomerate Φ_{DC}; here the conglomerate's members are instead in reversible partition equilibrium (H_{leq}) and are excluded by degree, and the irreversibility that does the work is that of covalent substitution together with H_{ret}. Theorem 2.5, which rests on the same $d^{*} \to \infty$, is superseded in the same way. Theorems 2.8–2.11 are not addressed.

Ruling 13.3 (Against Ch. 2, Thm. 2.12)**.** A Corrected. A Metropolis chain on a lattice is not a W_2 gradient flow; a reversible exchange at fixed degree is a gradient flow in Maas's metric; the driven source dynamics is not a gradient flow of any free energy.

Ruling 13.4 (Against Ch. 2, §§2.3.1 and 2.3.3)**.** A Superseded, and a reading corrected. I is C_s, so arm count replaces C_{2h} symmetry as the separation criterion. Moreover §2.3.3 gives Φ_{DC} hydrophilic substituents, whereas this paper's $\mathcal{D}$ carries no polar arm (H_{bulk}, H_{sel}); the two sets are therefore not identified, and Definition 4.13 does not import the monograph's Φ_{DC}.

Ruling 13.5 (Against Ch. 2, §2.2.2)**.** A Replaced. $\{3, 6, 9, 12\}$ is the terminal degree of a kinetic chain, not asserted to be a free-energy minimum. The monograph's heterogeneous intercalation interleaves $\Psi_{6,12}$ and $\Psi_{3,6,12}$ within the tetrasubstituted lattice; here the intermediate is nearly absent from the exported stream ($p_3 \approx 4.88 \times 10^{-4}$), so the structure is replaced by the composition vector (p_n) rather than reproduced by it.

Ruling 13.6 (Amending Article 65 §4: clause (i))**.** A Article 65's documentary bundle H_{mat} is a closed list of clauses by figure, which later papers cite in place of the filing [Sch26d, Hyp. 4.1, §4]. It is amended by one clause:

> (i) Figure 12 of the filing exhibits the formation of substrate and catalyst and the experimental results of those syntheses: LCMS, NMR and mass spectra of the 6,12-disubstituted catalyst and of its phosphorylated form; LCMS, NMR and UV/Vis of the 3,6,9,12-substituted substrate; and LCMS of the π-stacking of phosphorylated and non-phosphorylated catalyst. Its description reports a four-day bromination of chrysene by Br_2 in which the 6- and 12-positions are brominated first and simultaneously and the 3-position next, and names oxalate and hydroxyethoxy side chains.

Clause (i) is E as to wording and enters no proof, as Article 65 requires of every clause of its bundle [Sch26d, Hyp. 4.1]; what it does is move the bromination sequence, (K1) and the oxalate arm into column A, and a clause can do nothing else. The panel assignments follow the filing's brief description, whose labelling of panels 12(j)–(k) is not internally consistent; nothing here rests on which panel shows which spectrum. The amendment is required because clauses (a)–(h) do not cover Fig. 12, so without it the bromination sequence would carry the mark S.

Ruling 13.7 (Against Article 65, Table 1, polarity column)**.** D Recorded, open. Article 65 marks D, T, I apolar, meaning that they partition into a bilayer rather than the lumen. This paper requires a volumetric aqueous stock phase (H_{phase}), which Propositions 5.3, 8.11 and 10.15 and Theorem 8.8 all use. The earlier suggestion that an interfacial or lamellar phase reconciles the two is withdrawn: it is incompatible with the diffusion estimate this paper itself makes. The conflict stands as Target 14.5.

Ruling 13.8 (Against Article 65, block V2, the initiator)**.** D Corrected here. Article 65's Theorem 7.3 counts the initiator among the four species "the architecture consumes and does not make", and its block V2 gives the polymerisation edge as $Nt + I \to St$. The initiator is therefore a per-period demand, $c_I \geq 1$, not a founder quantity, and Definition 10.1 and Corollary 7.4 are stated accordingly. Article 65's Remark 7.2, that the initiator is "retained" at polymerisation, is not read against this: its subject is that retention is not *production*, so that the initiator stays in the source set—the same conclusion.

Ruling 13.9 (Article 77)**.** C Consistent; no amendment proposed. Article 77 admits by substitution family with a full constitutional specification, and allows arms as specified finite graphs [Sch26a, §3, Def. 3.1]; its Table 2 is a concrete catalogue of choices within those families, not the predicate itself. The arms o and e_P are specified finite graphs, so Theorem 10.7 holds against the predicate as written and the source needs no widening of it. Article 77's own allocation criterion (M3) carries the per-use fitness (H_{acc}). Two of its open obligations are used here and remain open: the four-carbon complement of a route-A membrane from $D2$ (Prop. 3.10) and the certification of allocation supports (Def. 3.7).

Ruling 13.10 (Article 2, Article 39, Article 40)**.** D Resolved in part. Article 40 is the second restatement of the formalism and supersedes the earlier axiomatic Article 2 [Sch26b]; Article 39 is a distinct editorial review and is not an axiomatic source. This paper cites Article 40 for Axioms A2, A3 and A12, for the non-implications, and for Target 49, and those citations resolve there. Article 78's citations of "Article 39" resolve unevenly: its Theorem 8 and Axioms A_6–A_7, A_9 match Article 40, while its Λ_{crit} and $\hat{\Pi}$ stacking operator, cited as "Lemma 11", do not—Article 40's Lemma 11 is the disjointness of primary and dual locant supports. No result here depends on Λ_{crit}. Which source carries it is Target 14.11.

Ruling 13.11 (Articles 62, 78)**.** A Consistent. Article 62's pool ratio ν and route-A lipid stoichiometry and Article 78's supply equation are used unchanged, and Article 78's bilayer demand (its Prop. 9.1) is now carried in R_D. Where Article 78 describes its incoming units as PDG-substituted and its linker as a phosphodiester bridge, this paper's e_P is the monoester precursor of that bridge, not the bridge itself. Article 78's pool at $L = 200$ and Article 65's differ; this paper uses Article 65's.

14 Targets, and conclusion

Target 14.1 (Rate magnitudes)**.** Measure or compute $k_1, \ldots, k_4$ and $e_0, \ldots, e_4$ for the bromination–oxalate–reduction route; in particular e_3/k_4 and the resulting k_4/k_3 against Proposition 7.5, and k_3/e_2 against Theorem 7.2.

Target 14.2 (Per-arm enhancement, and its magnitude)**.** Measure q for the bulk/stock pair, and separately establish that e_n at $n = 2$ is large enough for export to compete with the next substitution at all. The theorems use the ordering and the ladder; the absolute scale is a distinct requirement.

Target 14.3 (Selectivity of the arming chemistry)**.** Establish H_{sel}: that the other polyaromatics of the bulk are not armed on the horizon, and that bromination of chrysene at 6 and 12 outruns their functionalisation.

Target 14.4 (Capacity-limited bulk)**.** Extend the chain to a bulk in which resident T competes with I for reagent or export sites, so that e_4 enters the composition (Remark 7.7).

Target 14.5 (Identity of the stock phase)**.** Identify σ and reconcile it with Article 65's polarity column. The theorems here require a volumetric aqueous phase (H_{phase}); a lamellar or interfacial phase would require them to be restated.

Target 14.6 (Registry)**.** Measure Δ_{rgy}, the free energy of one arm registration, and confirm $\nu = 4$ and 2 for the tetra- and disubstituted stacks. The quantity is the difference between the stacking constant of a registering pair and that of a matched non-registering guest, and it is what decides whether the third stage of Scholium 8.14 is worth anything.

Target 14.7 (Competitors of other ring counts)**.** Proposition 4.4 bounds the four-ring polyhexes only. Determine whether any polyaromatic of another ring count presents a registering four-point pattern, and if so what ν it achieves.

Target 14.8 (Stacking and residence)**.** K, K', K'' for the admitted stock, chrysene and a representative member of $\mathcal{D}$; whether $K_{DT} = K_{DD}$ (H_{stack}); the return barrier Γ_n that H_{ret} asserts to be large, and the delivery time scale it must be compared with.

Target 14.9 (Acceptance sets)**.** Confirm, use by use, the arm words each downstream function accepts (H_{acc}), in particular which arms of the transformed tetrasubstituted unit must carry e_P, and discharge Article 77's four-carbon obligation for a route-A membrane from $D2$.

Target 14.10 (The waste class)**.** Decide whether the monosubstituted exports accumulate in σ, where Theorem 9.4 leaves them and where they add to the column impurity of Theorem 8.3, or are removed by a declared channel.

Target 14.11 (Corpus citations)**.** Settle which source carries Λ_{crit}, the $\hat{\Pi}$ stacking operator and "Lemma 11" as cited by Article 78, given that Article 40's Lemma 11 is a different statement and Article 39 is an editorial review.

Proposition 14.12 (What is established)**.** [A] *Subject to Appendix A: (i) substitution-initiated export has a closed-form exit distribution (Thm. 6.4); (ii) under the author's kinetics one design equation matches the stream to the demand, with an explicit efficiency bound and, at the illustration and with the initiator condition satisfied,* $\eta = 0.998437$ *(Thms. 7.2, 7.3, Cor. 7.4); (iii) the kinetic price of that match is the trade-off* $k_4/k_3 = q\rho^*/(x(1+x))$ *(Prop. 7.5), and slow completion is the regime to avoid (Prop. 6.9); (iv) column impurity is quadratic in the stacking ratio (Thm. 8.3), and exponentially small in the arm registrations a guest breaks (Cor. 8.6), the substitution pattern being unavailable to any four-ring competitor (Prop. 4.4, Cor. 4.5); (v) with returns disallowed the bulk empties, the admissible stock retains its weight and the low-degree exports are isolated (Thm. 9.4, Cor. 9.5), while returns would drive the stock to full substitution (Prop. 9.7); (vi) selectivity against the background is four filters, of which the arming step need not be one, and registry is the only one that protects the disubstituted stream (Sch. 8.14, Cor. 8.6); (vii) admission is independent of the arm law under Article 77's predicate as written (Rem. 10.6, Thm. 10.7), and cleaved arms cost efficiency only (Prop. 10.11); (viii) the carbon ledger closes upstream with oxalate as the only incorporated carbon reagent (Prop. 10.13); (ix) diffusion can fail to bind delivery only below an explicit ceiling on the stacking constant (Prop. 10.15).*

Remark 14.13 (What is not established)**.** [A] No rate is derived: the bromination sequence is attested, its magnitudes are not, and those of the oxalate substitution, the reduction and the export are stipulated illustrations. No mechanism is given for the cooperativity that (K3) requires. The stability of arm identity (H_{arm}), the identity of the stock phase (H_{phase}), the registry factorisation (H_{rgy}) and the no-return premise (H_{ret}) are stipulations; no value of Δ_{rgy} is supplied, and the polyhex enumeration covers four-ring species only. The selectivity of the arming chemistry (H_{sel}) is also a stipulation, but an optional one: it is named where used and no result requires it. Theorem 9.4 covers the classical sector and a partial instance of A12. The binding step of delivery is not identified.

Scholium 14.14 (What would overturn the paper). Three findings, in order of likelihood. A transfer free energy that does not fall with arm count, or a return barrier that rises with it, would leave the chain intact and remove its cause: chrysene would be armed and stay in the bulk. A fourth substitution slower than the export of the trisubstituted unit would leave every identity standing and move the source into the bottleneck regime, where the tetrasubstituted demand costs orders of magnitude more bulk than the disubstituted one. A stock phase from which admitted units return on the time scale of a period would replace the matched composition by the full-substitution limit of Proposition 9.7. And a registration free energy near zero would remove the one filter that separates an armed competitor from the stock at degree two, leaving the disubstituted stream protected by the arming step alone and so returning the paper to the premise it was written to avoid. These are a partition measurement, a rate ratio, a residence time and a difference of stacking constants.

A Hypothesis register

The register is Table 1.

Remark A.1. [A] Five premises carry most of the weight and none is attested: H_{trans}, which turns a partition ladder into a rate ladder; (K3), which demands cooperativity; H_{ret}, which makes the separation stand; H_{phase}, which four results require; and H_{rgy}, which carries the only filter that protects the disubstituted stream against the background. A reader allocating scepticism should spend it there, and not on H_{sel} and H_{bulk}, which are marked optional because the restatement of Proposition 8.11 removed every result that needed them.

B Verification

Script `verify_source.py` (Python standard library; exact rational arithmetic except V3, the Perron value in V8, and V10). It writes `verification_values.tex`, which this paper inputs; no number in the body is typed by hand. Rate parameters are stipulated nondimensional illustrations; physical constants in V10 are stipulated and marked [E].

V1 Adopted kinetics: $q = 10$, $e_n = 0.01q^n$, $k_1 = k_2 = k_4 = 100$, $k_3 = 5.40 \times 10^{-3}$ from the design equation. Closed form equals the fundamental matrix exactly; $\sum p_n = 1$; $p_2/p_4 = R_D/R_T$ and $c_I \le \Phi_{\min} p_3$ asserted exactly; $\eta_{DT} = 0.998413 \ge 0.998411$ and $\eta = 0.998437$; $\Phi_{\min} = 42{,}630$; initiator made 20.8; mean residence 1.014; the cooperativity identity of Prop. 7.5 asserted at $x = 0.1, 1, 10$ with the exact re-matched p_3.

V2 Contrast (slow completion): $(k_1, \dots, k_4) = (2, 1, 0.002, 0.001)$; $p_4/p_3 = k_4/e_3$ asserted exactly; window threshold 8.10; completion threshold $k_4/k_3 \ge 90$ for $p_4 \ge p_3$.

Table 1: The hypothesis register. Marks: A attested by a clause of H_{mat} as amended (Ruling 13.6); S stated by the author.

	Premise	What rests on it	What survives its failure
H_{in}	Chrysene present in the bulk	Every quantitative statement	The conditional form of every theorem
H_{seq}	Arming prompt relative to export (S)	The degree advancing at bromination rates; e as the exported arm	Everything, with o-armed exports and the same carbon count
H_{cat}	Oxalate substitution proceeds; catalyst carbon-free (S)	Def. 4.7; Prop. 10.13	The chain, with another arming route
H_{sel}	$\mathcal{D}$ not armed (S, *optional*)	The magnitude of c_d^{σ}, hence H_{bulk} and Prop. 5.3	Everything; Prop. 8.11 is stated in c_d^{σ}
H_{arm}	Arm identity stable (S)	Thm. 10.10; H_{acc}	Prop. 10.11 with larger π_h
H_{phase}	σ volumetric, β mobile (S)	Props. 5.3, 8.11, 10.15; Thm. 8.8	The chain and the scission theorems
H_{loc}	All substitution in β	Def. 6.2; Thm. 9.4(b)	The two-zone variant, Prop. 7.9
H_{cov}	Substitution irreversible	Thm. 9.4; Props. 9.7, 10.17	Thm. 6.4 as a first-passage law
H_{ret}	No return from σ (S)	Thm. 9.4; Conv. 2.3	Prop. 9.7 describes what happens instead
H_{add}	Arm additivity, $q > 1$	Thms. 5.1, 6.7; Props. 5.3, 6.9	Thms. 6.4, 7.2, 7.3 with general e_n
H_{trans}	Ladder on the forward rate (S)	Thm. 6.7; Props. 6.9, 7.5	The same three theorems with general e_n
H_{bulk}	$P_d \le P_0$ (*optional*, under H_{sel})	Thm. 5.1's second clause; Prop. 5.3	Thm. 6.4; Prop. 8.11 as restated
H_{reg}	Order along $\mathcal{P}$ (6,12-then-3 A; the rest S)	Def. 6.2; Thm. 10.7	Prop. 6.5's bound
H_{kin}	Author's kinetics; (K1) A, (K2)–(K4) S	Cor. 7.4's magnitudes	All identities; Props. 6.9, 7.5
H_{rgy}	Arm registry; $K'/K = e^{-\Delta_\pi} e^{-\nu\Delta_{\mathrm{rgy}}}$ (S)	Cor. 8.6; stage 3 of Sch. 8.14	Thm. 8.3 with K' free
H_{stack}	Common stacking constant (S)	Prop. 8.11 for the T stream	Thm. 8.3 for D alone
H_{leq}	Impurity partition equilibrium	Prop. 8.11	Thm. 8.3
H_{acc}	Acceptance sets (S)	Thm. 10.10; Prop. 10.11	Thm. 10.7

V3 Two-zone variant: the $T = I$ crossing by bisection; $r\delta \to x^* = 1.5936$, error $\approx 1.8/r$.

V4 Article 65's demand reproduced; the ICL bilayer term; R_T with the pore per founder; ρ^*.

V5 Contrast throughput 1.2×10^9, efficiency 3.7×10^{-5}.

V7 Carbon per unit $D2 = 22$, $I2 = 24$, $T2 = 26$, $T0 = 18$, $Dm = 20$; the formula with oxalate and phosphate arms checked against Article 77's Table 2 and both balances at every arm count; carbon in the delivered demand 937,196; carbon in the initiator made 499 and in the initiator drawn 24; declared four-carbon coproduct 26,708.

V8 Column impurity: exact finite-column sums at $\ell = 10, 50, 200, 400$; Richardson extrapolation against the Perron limit (relative agreement better than 0.5%); the bound and the first-power estimate.

V9 Arm-word counts by Burnside, confirmed by enumeration for two and three arm types; arm efficiency at $\pi_e = 0.99, 0.95, 0.90$.

V10 Delivery: $D_{\mathrm{m}} = 5 \times 10^{-10}\,\mathrm{m^2 s^{-1}}$, $R_v = 10\,\mathrm{nm}$, $\delta T = 12\,\mathrm{h}$, with Avogadro's number carried explicitly.

V11 Residence: an exact linear solve equals the closed form at $r = 10^{-3}$, $a = 5$, $d = 0.05$.

V13 Registry: the suppression $e^{-2\nu\Delta_{\mathrm{rgy}}}$ at $\nu = 2, 4$ and $\Delta_{\mathrm{rgy}} = 1, 2$, and the resulting impurity bound at the V8 composition. Floating point.

V12 Scission under H_{ret}: the admissible and waste limits 0.998901 and 1.10×10^{-3}; the bulk decay rate $\lambda_* = 1.005$; for the open source, $(-G)\tau = \mathbf{1}$ with an exact positive solution on $\{\beta\} \cup \Omega_{\mathrm{adm}}$ (M-matrix certificate, maximum 101); and the counterfactual residual 9.9×10^{-8} that returns would produce.

C Molecular commentary, isolated

Remark C.1 (Status). A Nothing here enters a numbered statement.

Remark C.2 (The filing). E The three substitution families appear together (Fig. 4; clause (a)), with their conversion to nucleotide pairs (Figs. 6–7; clause (c)), to tethered anchors (Fig. 9(b); clause (d)) and to the membrane relation of the 6,12-disubstituted unit (Fig. 16(b); clause (f)). Clause (i), added by Ruling 13.6, carries Fig. 12: the synthesis and experimental characterisation of catalyst and substrate, and a four-day bromination of chrysene by Br_2 in which the 6- and 12-positions are brominated first and simultaneously and the 3-position next. That sequence is the documentary basis of H_{reg} and of (K1). It attests no rate magnitude, and the filing's bromination was carried out in solution rather than in a polyaromatic bulk, so H_{loc} is not attested by it either.

Remark C.3 (The arming route, and its tension). E Electrophilic bromination of chrysene at the 6- and 12-positions

is the step the filing reports, and it is consistent with the usual reactivity of those positions. The subsequent steps are not: replacement of an aryl bromide by an oxygen nucleophile and reduction of an oxalate ester to a glycol ether are each ordinary transformations, but they are not electrophilic aromatic substitutions, and the paper does not supply their conditions. Two tensions are recorded rather than resolved. First, oxidative functionalisation of chrysene is usually reported at other positions, so the regiochemistry here depends on the bromination step carrying the selectivity, as the filing reports it does. Second, if an e-arm is in practice reached through the phenol, then h is an obligatory intermediate, $\pi_e = 1$ is a complete-conversion limit rather than a reagent choice, and Proposition 10.11 rather than Theorem 10.10 is the operative statement.

Remark C.4 (Calcium oxalate as a buffered source)**.** E A sparingly soluble salt holds the oxalate activity nearly constant while it is consumed, which is the behaviour Definition 4.13(c) assumes of the reagents. No solubility value is used anywhere in the paper.

Remark C.5 (Chromonic analogy)**.** E Planar aromatics with ionic or strongly polar side groups form columnar stacks in water with a rise near 0.34 nm, matching the ICL stacking span of Article 78 (its Def. 5.2). Such assembly is well described by the isodesmic model [ZC22], which is the form Theorem 8.8 uses; no constant is imported.

Remark C.6 (Group contribution)**.** E Additivity of fragment contributions to partition coefficients is standard in solvation chemistry and is the empirical form of H_{add}; its accuracy for multiply-substituted planar aromatics, and the absolute magnitude of e_n, are Target 14.2.

D What was withdrawn in preparing this paper

Remark D.1 (The crossing constant)**.** A A first form of Proposition 7.9 stated $r\delta(r) \to 2$. V3 returned $r\delta = 1.59$ at $r = 1000$: the intermediate has not reached its quasi-steady value when T meets it, so the balance is $bt = 2(1 - e^{-bt})$.

Remark D.2 (The column exponent)**.** A Draft v0.1 stated column impurity $\leq (K'c_B)/(Kc_A)$. An interior impurity pays two mismatched contacts, so the leading factor is $(K'/K)^2 c_B/c_A$; the first-power form overstates impurity about fivefold at the sample values.

Remark D.3 (The divided stream)**.** A Draft v0.1 admitted a new mechanism, a divided stream held to full conversion, to escape the bottleneck. Under (K3) the bottleneck regime is not entered, so the mechanism is not forced and is withdrawn.

Remark D.4 ("The tetrasubstituted stock binds")**.** A Draft v0.1 presented this as a finding. It holds only under slow completion and is now the regime to avoid.

Remark D.5 (Corrections from the review of v0.3)**.** A (i) The carbon ledger credited resident cores at eighteen carbons, omitting their arms. (ii) The efficiency quoted was η_{DT}, not η. (iii) "Exactly $p_0 + p_1$" for the admission loss became "at most $p_0 + p_1 + 4\epsilon_{\mathrm{off}}$". (iv) The column-limit proof gained the end-letter factor that produces the $O(1/\ell)$ error, and the condition $K' > 0$. (v) The crossing proof gained the uniform convergence of G'_r.

Remark D.6 (The widened admission predicate, and the arm-catalogue obstruction)**.** A Drafts v0.3 and v0.4 held that Article 77's Table 2 was its admission rule, inferred an obstruction—that independent arm attachment produces units outside the list—and proposed a widened predicate in response. The premise was a misreading. Article 77 admits by substitution family with a full constitutional specification and allows arms as specified finite graphs; its Table 2 is a catalogue of choices within the families. The obstruction does not exist, and the proposed widening would have *narrowed* the predicate, since it dropped the finite assemblies, the optional 2,5,8,11 family and arm graphs outside $\{h, e, e_P\}$, Article 78's PDG arm among them. Proposition "Obstruction for the original catalogue", Definition "Widened admission predicate", Theorem "Admission without scheduling" and the hypothesis H_{sched} are all withdrawn; what replaces them is Remark 10.6 and Theorem 10.7, which reach the same conclusion—admission does not depend on the arm law—against the predicate as Article 77 already writes it. The arm-efficiency figure of 0.833 reported in draft v0.2, computed with the pore drawn every period, is withdrawn with them.

Remark D.7 (Open and closed sources)**.** A Draft v0.4 proved decay for an open source in which returns were permitted, and a positive residual for a closed one, and

offered the first as a discharge of Target 49. With returns permitted the open source empties every state, admissible ones included, so the statement separated nothing; and permitting returns breached Article 77's carbon boundary, since a returned admitted unit would be armed again. Both are replaced by H_{ret} and Theorem 9.4, in which the admissible weight is retained and the waste class is isolated, with Proposition 9.7 recording what returns would do. The earlier Q_{rej} omitted the degree-0 and 1 stock states and is corrected in Definition 9.1; the A12 instance is now declared partial, since the spectral realisation of its item 1 is not supplied.

Remark D.8 (The delivery converse)**.** [A] Draft v0.4 concluded from $K \le K_{\max}$ that diffusion does not bind, and carried a sufficiency clause in the proposition. The Smoluchowski rate is an upper bound on capture, so only the necessary direction follows, and the realised free monomer concentration may lie far below $1/K$. Both are withdrawn; the claim that membrane entry is the binding step goes with them.

Remark D.9 (The initiator and the stock phase)**.** [A] Draft v0.4 suggested the initiator might be a founder quantity; Article 65's edge π consumes it each period, so $c_I \ge 1$ and the condition $c_I \le \Phi_{\min} p_3$ is now carried explicitly. Draft v0.4 also offered an interfacial or lamellar stock phase as a way of reconciling Article 65's polarity column; that is incompatible with this paper's own diffusion estimate, so the reconciliation is withdrawn and the conflict is recorded as open.

E Sources, by use

The concordance is Table 2.

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[Sch26b] Charles D. Schaper. The Chrysene Formalism: Axiomatic Foundations of a Discrete Non-Commutative Topological Space. *Annals of the Chrysene Formalism*, 1(1):6–14, 2026. Article 2. DOI: https://doi.org/10.68366/vj2yay51. Superseded by A40, where it is cited as [Sch26c].

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Table 2: Sources, by use.

Source	Used at	What is taken
Monograph Vol. 5, Ch. 2	§13	The purification narrative (§2.8.1); the trajectory of §2.2.2
Article 2, Article 40	§3, §4.2, §9	A2's C_{2h} reference and A3's locants; the four-ring polyhex classification and its narrowed scope; A12; the non-implications; Target 49
Article 62	Def. 10.1	ν and its swept range; one route-A lipid per dimer
Article 65	Def. 10.1, §13	The demand; the species notation; the documentary bundle and citation rule; the initiator edge
Article 77	§4, §10	The admission predicate and arm specification; Prop. 3.2 and the monoester balance; the open balance (M2); the allocation criterion (M3); Props. 3.10, 3.12, 9.3
Article 78	Def. 10.1, Prop. 10.15	n_{supply}; the bilayer demand of Prop. 9.1; the period; the flip-flop target
US 12,195,423	App. C	Via Article 65's bundle as amended: clauses (a), (c), (d), (f) and the new clause (i)

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