ACS SYMPOSIUM SERIES **297**

Chromatography and Separation Chemistry

Advances and Developments

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CIBA-GEIGY Corporation

Developed from a symposium sponsored by
the Division of Analytical Chemistry
at the 188th Meeting
of the American Chemical Society,
Philadelphia, Pennsylvania,
August 26–31, 1984

American Chemical Society, Washington, DC 1986

Library of Congress Cataloging in Publication Data

Chromatography and separation chemistry.
(ACS symposium series, ISSN 0097-6156; 297)

"Developed from a symposium sponsored by the Division of Analytical Chemistry at the 188th Meeting of the American Chemical Society, Philadelphia, Pennsylvania, August 26-31, 1984."

Includes bibliographies and index.

1. Chromatographic analysis—Congresses.
2. Separation (Technology)—Congresses.

I. Ahuja, Satinder, 1933- . II. American Chemical Society. Division of Analytical Chemistry. III. American Chemical Society. Meeting (188th: 1984: Philadelphia, Pa.) IV. Title. V. Series.

QD79.C4C4838 1986 543'.089 85-28694
ISBN 0-8412-0953-7

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PRINTED IN THE UNITED STATES OF AMERICA

ACS Symposium Series

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FOREWORD

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PREFACE

CHROMATOGRAPHY IS A POWERFUL SCIENCE concerned with separations of a large number of complex compounds. The contributions of chromatography to various scientific disciplines remain unmatched as is exemplified by the progress made in biological sciences such as biotechnology, clinical pharmacology/therapeutics, and toxicology. This book was planned to compile some of the exciting developments in the science of chromatography and separation chemistry.

A unified theory recently proposed to explain the manner of sorption and the form of sorption isotherm in gas, liquid, and ion-exchange chromatography is presented in some detail. Selectivity in reversed-phase high-pressure liquid chromatography is explored at length. Several chapters deal with characterization of bonded phases, relationship of column-packing structure and performance, variability of reversed-phase packing materials, and the differences between silica-based reversed-phase and poly(styrene–divinylbenzene) columns. A short review is included to cover various approaches used in HPLC to achieve the desired selectivity for resolution of enantiomeric compounds.

Detectors provide another route to optimizing selectivity by enhancing detectability of various classes of compounds. Discussion is included that describes the noise sources in optical detectors that allow optimization of such detectors. Two additional chapters deal with new and potential detectors including laser fluorimetry for HPLC, microcolumn HPLC, and FIA.

Effective use of computerization in chromatography is further advancing this science. Detailed information is provided regarding calculation and prediction of retention data for isocratic separations that allow optimization of methodologies. Calculation of retention data for complex gradient elution is also shown.

Recent developments in separation science are covered from the standpoint of their impact on various modes of chromatography. Chromatographic applications of cyclodextrin and phenylboronic acid stationary phases are discussed. The renaissance in electrophoresis has given risen to high-resolution, two-dimensional gel electrophoresis. The basic methodology and recent advances are provided for studies on protein separations. Finally, the combination of capillary supercritical fluid chromatography and mass spectrometry is discussed as another powerful tool for separation and detection of a variety of compounds for which GLC and HPLC cannot be used because of their apparent shortcomings.

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May 20, 1985

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Manner of Sorption and Form of the Sorption Isotherm in Gas, Liquid, and Ion-Exchange Chromatography

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The Langmuir model of sorption and isotherm relation are discussed in terms of approximations made in their formulation. An elemental modification of the latter is shown to yield an equation that, in principle, accounts for adsorbate asymmetry, surface heterogeneity, multilayer formation, and sorption-desorption hysteresis and, hence, that encompasses the BET model and isotherm Types 0 through V. Summation extension yields a comprehensive equation with which stepped isotherms can also be represented. The form of the latter is used to describe retentions in gas, liquid, and ion exchange chromatography; the powers and coefficients of the resultant expressions are shown in the first and third of these cases to be rigorously interpretable in terms of the solute activity and partition coefficients.

The method employed for choosing appropriate systems and conditions for a particular analytical-scale chromatographic separation has traditionally amounted to maximizing the column efficiency and, at the same time, choosing (often nearly at random) stationary and/or mobile phases that are thought to be suitable for the sample at hand (optimizing the system selectivity). Maximizing the efficiency of chromatographic systems is taken to be well understood at the present time, at least in principle (e.g., 1); even so, while this method of effecting separations is straightforward and in fact frequently provides a satisfactory solution, very many instances are encountered wherein, if for no other than practical reasons, the selectivity of the system must be enhanced as well. However, given the paucity of quantitative guidelines regarding the latter, decisions made pertaining to appropriate experimental conditions and technique(s) with which to achieve this end have in the past inevitably been based primarily upon the experience of the analyst as guided by what literature reports there might be that describe ancillary analyses (e.g., 2).

An alternative approach to optimizing the system selectivity, and one more rational than that of trial-and-error, would appear to be understanding, first, of the physicochemical basis of chromatographic separations (3-7); followed by modeling of the system at hand; thence optimizing the system and conditions within the boundaries of whatever level of resolution is sought (8;

0097-6156/86/0297-0001$09.25/0

see the reviews 9,10). However, while the third of these areas is now adequately characterized, the first and second remain only poorly understood since, presupposed, is a knowledge of the physicochemical interactions that take place between the solute and the mobile and stationary phases, as well as those that may occur between the mobile and stationary phases themselves. These may, in addition, be interdependent. Any model of the selectivity of the chromatographic process must therefore take account of such interactions; one such theory, founded upon a modified form of the Langmuir model of sorption, is formulated in what follows.

GENERALIZED REPRESENTATION OF ISOTHERM TYPES

The Langmuir Model

The pioneering consideration of isotherms, including their representation and interpretation, was carried out by Langmuir at the turn of this Century (11). His model is that of a symmetric adsorbate (solute) that interacts with an adsorbent comprised of S uniform sites such that the solute becomes attached to (adsorbs on) the solid surface. The process is said to result in S_1 sites of the adsorbent becoming occupied, leaving S_o sites unoccupied, where

$$S = S_o + S_1 \tag{1}$$

is presumed to obtain.

The rate at which sites are vacated (i.e., the rate of adsorbate evaporation from the surface) is said to be given by k_1S_1, whereas the rate at which sites become occupied in the first place (i.e., the rate of adsorbate condensation) is $k_2\ p_A S_o$, where k_i are rate constants, and where p_A is the partial pressure of adsorbate above the adsorbent. Thus, at equilibrium,

$$k_1\, S_1 \;=\; k_2\, p_A\, S_o \;=\; k_2\, p_A\, (S - S_1) \tag{2}$$

Now let Θ be the fraction of sites occupied at any time:

$$\Theta = S_1/S \tag{3}$$

Then, upon substituting equation 2 into 3, followed by rearrangements,

$$\Theta = \frac{k_2\ p_A}{k_2p_A + k_1} \tag{4}$$

Letting $b = k_2/k_1$, the ratio of the rate constants (i.e., an equilibrium constant) which is taken to be independent of p_A,

$$\Theta = \frac{b\ p_A}{1 + b\ p_A} \tag{5}$$

Alternatively, Θ can be replaced by the volume ratio v_A/V_A, where v_A is the volume of adsorbate actually on the surface, and where V_A is the volume of adsorbate corresponding to monolayer coverage: $\Theta = v_A/V_A$. Also, since the density of the adsorbate is assumed to be unaffected by the adsorption process, Θ could equally be represented by a mole or weight ratio.

The denominator of equation 5 tends to unity at very low pressure, whence $v_A = b\ V_A\ p_A$; plots of v_A against p_A are then predicted to be linear and of zero intercept. When in contrast $(b\ p_A)$ is not negligible in comparison with unity, the plots are predicted to be curved concave to the abscissa, i.e., the well-known Langmuir isotherm.

The BET Model

In practice, isotherm plots are of course found to describe a number of forms different from those mentioned above. Each has become known as a Type, where Type 0 is the ideal (i.e., linear) case, followed by Type I, the Langmuir isotherm. Examples of Types II-VI are also known, Brunauer, Emmett, and Teller (12) being the first to collate systems that exhibit such curve shapes.

These workers were also the first to model multilayer sorption: the Langmuir assumption of a uniform surface is retained; further, solutes in the first layer are said to be localized to (i.e., immobilized on) a given site. Additional adsorbate molecules are then permitted to stack (but not interact) in layers on top of one another, where molecules in the second and subsequent layers are taken to have properties approximating those of bulk condensate. The resultant formulation with which isotherms of at least through Type V can be reproduced is then given by:

$$\Theta = \frac{(c/p_A^o)\ p_A}{(1 - p_A/p_A^o)\left[1 + (c - 1)p_A/p_A^o\right]} \tag{6}$$

where c, a dimensionless constant greater than or equal to unity, is approximately $\exp(H_1 - H_L)/RT$, that is, reflects the (temperature-dependent) difference in the heats of sorption of the first and subsequent layers of adsorbate; and where p_A^o is the bulk-solute vapor pressure.

[The more familiar form of the BET equation can be obtained by substitution of v_A/V_A for Θ, followed by rearrangements:

$$\frac{p_A/p_A^o}{v_A(1 - p_A/p_A^o)} = \frac{(c - 1)p_A/p_A^o}{V_A\ c} + \frac{1}{V_A c}$$

where plots of the left-hand side of the relation against p_A/p_A^o are predicted to be linear and from which both V_A and c can be evaluated, the former from the inverse of the sum of the slope and intercept, and the latter from 1 + the slope/intercept quotient.]

Extension of the Langmuir Model to Include Equation 6

As a prelude to application of the Langmuir formalism to chromatography, we first enquire whether some or other simple modification of it can accomodate the BET relation, equation 6, since, if so, the resultant generalized expression might then be indicative of an appropriate model of the sorption process relevant to analytical separations. Accordingly, we rewrite the Langmuir equation with b replaced by a second constant b' in the denominator of equation 5:

$$\Theta = \frac{b\ p_A}{1 + b'\ p_A} \tag{7}$$

where $b = c/p_A^o$, and where setting $(1 + b'\ p_A)$ equal to the denominator of equation 6 provides the identity:

$$b' = \frac{c - 2}{p_A^o} + p_A \left[\frac{1 - c}{(p_A^o)^2} \right] \tag{8}$$

whence b' is identified as being pressure-dependent.

The BET model is well-known to hold only in the limit of low pressure, so that equation 8 reduces approximately to:

$$b' \approx \frac{c - 2}{p_A^o} \tag{9}$$

When $c >> 2$, $b' \approx c/p_A^o = b$, whence equation 7 further reduces to equation 5, i.e., the Langmuir model, with which isotherm Type I is described. In the limit of sufficiently low pressure, the relation describes Type 0 as well, as discussed above. In those instances where $c \approx 2$, $b' \approx 0$ which results also in a Type 0 isotherm. When p_A cannot be neglected then, for $c >> 2$, isotherm Type II results, with the eventual appearance of the Type IV extension. In contrast, for $c \approx 2$, $b' \approx - p_A/(p_A^o)^2$ which yields isotherm Type III and, as p_A is increased, Type V. Equation 7 thereby accounts for the seemingly-inexplicable fact that stepped isotherms such as Types IV and V (the former being particularly common) are frequently observed at pressures far below that corresponding to saturation. (It is of interest in this regard that isotherm Type II is a composite of Types I and III, whereas isotherm Type IV is a composite of Types I + I. Similarly, isotherm Type V is comprised of Type III with extension to Type I.)

Comprehensive Isotherm Relation

The above derivations have been brought out in full in order to reveal the approximations made in each and, moreover, to illustrate that neither the Langmuir nor BET models account for multi-stepped isotherms despite modification of the form of equation 5. First, of course, adsorbate species of interest generally, let alone those in chromatography, self-evidently will rarely be of spherical symmetry. Thus, adsorbates can adsorb onto an adsorbent in different ways, for example, the hypothetical edgewise vs. planar adsorption of benzene onto a presumed-flat surface. In addition, not only can there be different conformations of the first layer of adsorbate on an adsorbent, but this layer may also orient the second layer, which in turn can orient the third layer, and so on. The phenomenon is well-known in the sorption of liquid-crystalline materials onto solid surfaces, the so-called "boundary layer" (that is, that which is intermediate between the surface and bulk liquid) being known to extend in some cases over thousands of Angstroms (13). However, the ordering is not necessarily unidirectional (nematic-like) and can in fact extend in two dimensions, analogous to two-dimensional ordering of smectic liquid crystals. (With chiral adsorbates, there could evidently be superposed a twist as well.)

The second major objection to the Langmuir and BET formulations derives from consideration of the adsorbent surface. Both models assume a finite number of uniform sites available for adsorption, but even cursory microscopic evaluation of surfaces of interest in chromatography demonstrates that with the possible exception of smooth glass beads, this is rarely the case. Surfaces such as diatomaceous earth, silica, etc. are highly heterogeneous and, in addition, possess microporous structure, the adsorptive properties of which can be much different from those of the surface (14).

Also implicit in the models is that the surface remains unchanged when contacted with an adsorbate. This is now known to be incorrect in at least several instances, and adsorbates can in fact cause a reorganization of adsorbent surface atoms (15).

Finally, because adsorbate molecules are adsorbed in a specific orientation (or array of orientations), there will be hysteresis involved in the sorption/desorption process (16). Hysteresis is known to arise also as a result of adsorbent-site heterogeneities (17).

In order to take account of all of the above effects, we rewrite equation 7 at this point as a summation:

$$\Theta = \sum_{i=1}^{n} \left[\frac{b_i \; p_A}{1 + b_i' \; p_A} \right] \tag{10}$$

where isotherm Types 0-V can be represented as described above with $n = 1$, while multi-stepped isotherm shapes require that $n \geqslant 2$ with $b_i \neq b_i'$. The alternative (but equivalent) view is a virial expansion of equation 8, the first three terms of which must evidently be:

$$b' = -\frac{1}{p_A^o} + \frac{1}{p_A^o}(c - 1) - \frac{p_A}{(p_A^o)^2}(c - 1) + \ldots \tag{11}$$

Multi-stepped isotherm shapes can therefore be described either by expansion, as required, of the summation of equation 10, or by virial extension of equation 11; while hysteresis is taken into account by replacing b_i in the denominator of equations 5 et seq. with b_i'. Moreover, in doing so, and in contrast to the BET model, each of the second and higher layers of adsorbate can be distinguished as is important, for example, in instances of liquid-crystalline solutes.

APPLICATION OF EQUATION 10 TO GAS CHROMATOGRAPHY

Generalized Representation of Retentions with Blended Sorbents

It has been shown in very many (but by no means all) instances of the use of binary stationary phases in gas chromatography, that solute partition coefficients at hypothetical zero column pressure drop K_R^o (i.e., corrected for virial effects; 18) are described by the relation (19-23):

$$K^{o}_{R(M)} = \phi_B\, K^{o}_{R(B)} + \phi_C\, K^{o}_{R(C)} \tag{12}$$

where the subscripts refer to pure stationary phases B or C or to a mixture of these (M = B + C), and where ϕ_i (i = B or C) is a volume fraction. In addition, Laub has described and discussed various modifications that can be incorporated into equation 12 to take account of solute-solvent stoichiometric or nonstoichiometric complexation along with concomitant solvent-solvent self-association and/or solvent-additive interactions (24; see also ref. 25).

In order to assess whether the isotherm formalism might be applied to these situations, we write equation 12, first, in the form:

$$K^{o}_{R(M)} = \phi_C \left\{ K^{o}_{R(C)} + \sum_{i=1}^{n} \left[\frac{b_i\, \phi_B}{1 + b'_i\, \phi_B} \right] \right\} + \phi_B\, K^{o}_{R(B)} \tag{13}$$

We then seek to interpret the constants b_i, b'_i in what follows.

Non-Interactive Solute Solution with Non-Interactive Solvents

In the trivial case of what might well be referred to as elemental solute solution in the stationary-phase blend M, there is presumed to be neither solute specific chemical interaction with B or C, nor stoichiometric or nonstoichiometric solvent-solvent chemical interaction. Thus, allowance is made for nonspecific solute interactions with M (such solutions being designated variously as ideal, athermal, "regular", "solvated", random contact-paired, and so forth, depending upon the enthalpy and entropy of mixing), while the solvent-solvent solution is taken to be ideal. The regression of solute partition coefficients against the solution composition in these instances will be linear, and will accordingly be described by equation 13 with b_i, b'_i set equal to zero, i.e., equation 12. Since the pure-phase partition coefficients will in all likelihood differ, the slopes of such plots may be positive, zero, or negative, examples of all of which have been documented and discussed (19-21).

We note also that solvent-solvent "ideality" is mimicked by systems that exhibit partial miscibility. Thus, equation 12 is expected to hold in these instances as well, since the compositions of each phase of such two-phase systems are invariant with the notional concentrations of B and C. In testing this, Laub, Purnell, and Summers (26) evaluated the partition coefficients of several solutes with the solvent systems tributyl phosphate/ethylene glycol and ethyl benzoate/propylene glycol (upper consolute temperatures of 53° and 47°C, respectively), and found that not only was equation 12 obeyed as expected within the two-phase regions of each but also, that the lines were contiguous with those corresponding to the single-phase portions of the phase diagrams.

[As one consequence of the "ideality" of partially-miscible solvent systems, the use of mechanical blends of pure-phase packings is favored in packed-column analytical separations since, in the absence of any substantial volatility of B and C, equation 12 must be obeyed exactly and, hence, retentions with blended phases can be forecast from those with the two pure solvents (8,27; see the reviews 9,10,22). The same holds also for the use of tandem-connected packed (28,29) as well as capillary columns (30,31), provided that the pressure drop across each is correctly taken account of (32,33).]

Interactive-Solute Solution with Non-Interactive Solvents

In the simplest of these situations, solute complexation with one of the stationary-phase components, say C, in admixture with presumed-inert (i.e., non-interactive) diluent phase B, the Gil-Av/Herling relation (34) is substituted into equation 12 to provide:

$$K^{o}_{R(M)} = K^{o}_{R(B)} + \frac{K^{o}_{R(B)}\, K_{AC}\, \phi_C}{\bar{V}_C} \tag{14a}$$

$$= \phi_C \left[K^{o,t}_{R(C)} + \frac{K^{o,t}_{R(C)}\, K_{AC}}{\bar{V}_C} \right] + \phi_B\, K^{o}_{R(B)} \tag{14b}$$

where K_{AC} is the notional solute (A) complexation constant with C,

$$K_{AC} = \frac{\bar{V}_C \left[K^{o}_{R(M)} - K^{o}_{R(B)} \right]}{\phi_C\, K^{o}_{R(B)}} \tag{15a}$$

which, for $K^{o}_{R(M)}$ linear in ϕ [as in the several systems considered for example by Martire and Riedl (35); see also the many systems cited in refs. 19-21], reduces to:

$$K_{AC} = \frac{\bar{V}_C \left[K^{o}_{R(C)} - K^{o}_{R(B)} \right]}{K^{o}_{R(B)}} \tag{15b}$$

where the true (i.e., uncomplexed) partition coefficient of A with C, $K^{o,t}_{R(C)}$, is defined by:

$$K^{o}_{R(C)} = K^{o,t}_{R(C)} + \frac{K^{o,t}_{R(C)}\, K_{AC}}{\bar{V}_C} \tag{15c}$$

and where $\bar{V}_C$ is the molar volume of C.

Setting equations 15a and 15b equal immediately yields equation 12 (the manner, in fact, in which it was first derived), while substitution of equation 15c into equation 12 then provides equations 14.

Solute complexation with one of the solvent components, here C, is also described by the isotherm relation, equation 13, with n = 1:

$$K^{o}_{R(M)} = \phi_C \left[K^{o,t}_{R(C)} + \frac{b_1 \phi_B}{1 + b_1' \phi_B} \right] + \phi_B K^{o}_{R(B)} \tag{16}$$

where equation 16 reduces to equation 14b (hence 14a) upon specification of the following identities:

$$b_1 = \frac{K^{o,t}_{R(C)} K_{AC}}{\phi_B} \tag{17a}$$

$$b_1' = \frac{\bar{V}_C - 1}{\phi_B} \tag{17b}$$

In instances in which the solute interacts stoichiometrically both with B and C, equation 14b is expanded to:

$$K^{o}_{R(M)} = \phi_C \left[K^{o,t}_{R(C)} + \frac{K^{o,t}_{R(C)} K_{AC}}{\bar{V}_C} \right] + \phi_B \left[K^{o,t}_{R(B)} + \frac{K^{o,t}_{R(B)} K_{AB}}{\bar{V}_B} \right] \tag{18}$$

In terms of the isotherm formalism this is:

$$K^{o}_{R(M)} = \phi_C \left[K^{o,t}_{R(C)} + \frac{b_1 \phi_B}{1 + b_1' \phi_B} + \frac{b_2 \phi_B}{1 + b_2' \phi_B} \right] + \phi_B K^{o,t}_{R(B)} \tag{19}$$

i.e., equation 13 with n = 2, where in addition to b_1 and b_1' given as above, b_2 and b_2' are identitified as:

$$b_2 = \frac{K^{o,t}_{R(B)} K_{AB}}{\phi_C} \tag{20a}$$

$$b_2' = \frac{\bar{V}_B - 1}{\phi_B} \tag{20b}$$

Equations 16 and 19 are indicative of the versatility of the form of the isotherm relation, equation 13, insofar as the latter provides for description of solute complexation with either (or both) of the solvent components of binary stationary phases. In addition, each of what might otherwise appear simply to be empirical fitting constants can be precisely interpreted (equations 17 and

20). Moreover, the relations can obviously be expanded to take account of multicomponent phases to the same extent that the diachoric solutions relation, equation 12, can be extended (36):

$$K^{o}_{R(M)} = \sum_{i=1}^{n} \phi_i \; K^{o}_{R(i)}$$

Equation 12 takes account as well of solute/stationary-phase partitioning in the instance of gas-solid chromatography since, in the absence of adsorbent-adsorbent interactions, (adsorbate) solute specific retention volumes are described exactly by the weight-average of the retentions with the pure adsorbents (37). This holds also in the instance of adsorbate/adsorbent charge-transfer complexation, i.e., equations 14 and 15 (38).

However, for binary-component liquid (or solid or interfacial) sorbent phases, plots of $K^{o}_{R(M)}$ against ϕ are predicted to be linear irrespective of whether the solute complexes with B (K_{AB} finite; K_{AC} zero), with C (K_{AC} finite; K_{AB} zero), or with neither (K_{AB}, K_{AC} each zero) or both (K_{AB}, K_{AC} each finite). That is, even though these various situations can be interpreted precisely in terms of the equations presented thus far, the isotherm formalism appears at this point to provide little advantage over the diachoric solutions equation in the speciation of solute complexation with non-interactive solvents.

Non-Interactive Solute Solution with Interactive Solvents

The two solvent components have thus far been assumed to be non-interactive, that is, to form ideal solutions. Since these are equivalent to those comprised of immiscible liquids, Laub and Purnell christened such systems as "diachoric" (partitioned volume) (20). That is, diachoric solutions are defined as those for which the solvent-solvent activity coefficients γ are unity and, hence, for which plots of solute partition coefficients against solvent composition must regress linearly.

For example, Martire and Riedl proposed some years ago that K_{AC} is calculable solely from the end-points of what amount to (straight-line) plots of equation 14a (i.e., equation 15b), provided that the two solvents are identical in all respects (yield ideal solutions) save that one or the other complexes with the solute (35). Such systems include chloroform with the stationary phases n-heptadecane + di-n-octyl ether, for which the activity coefficient $\gamma_{i(M)}$ of either solvent component (i = B or C) in the blend M (= B + C) was said to deviate from unity by at worst $\pm\, 0.00_7$ at $\phi = 0.5$ (where the observed K_{AC} was taken to reflect hydrogen bonding of the solute with the latter solvent).

When in contrast the solvent components somehow interact attractively or repulsively (i.e., exhibit negative or positive deviations from Raoult's law), the regression of $K^{o}_{R(M)}$ must be presumed to be affected also. However, the form that this might take has yet to be specified in any detail. Nevertheless, and in order that equations 12 et seq. might be applied to combinations of stationary phases that are of interest in solutions theories in general, and in analytical gas-liquid chromatography in particular, the effect of solvent-solvent interaction on solute/stationary-phase partitioning must be taken into account.