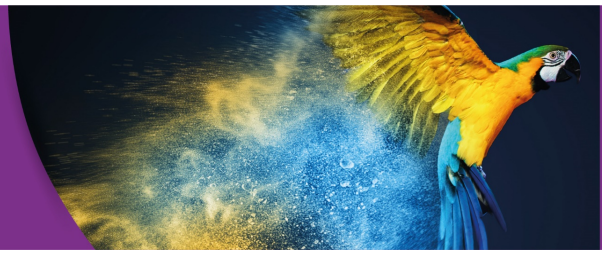


4. ASDC Dyeing Theory

4.1 Thermodynamics of Dyeing

4.1.4. Mathematical Interpretations of Equilibrium Adsorption data

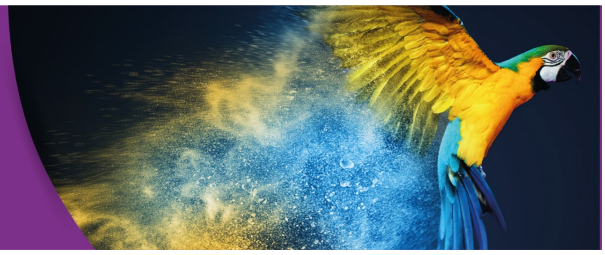
Learning Objectives for this section

- How can we describe real dye/fibre systems in terms of mathematical relationships that include thermodynamic parameters?
- What is the role of internal volume of a fibre when describing certain dye/fibre systems?
- How can we describe the behaviour of charged particles (anions and cations) within a dyebath at the surface of certain fibres?

Mathematical interpretations of adsorption equilibrium adsorption data

In the following discussion of the thermodynamic analysis of dye adsorption, the various dye-fibre combinations are divided into three groups based on their relative global popularity:

(i) non-ionic dyes/PET, CTA, CA fibres;
(ii) anionic dyes/cotton, CV, CLY fibres and;
(iii) anionic dyes/wool, silk and PA fibres, as well as basic dyes/PAN fibres.



Non-ionic dyes/PET, CTA, CA fibres

The thermodynamic analysis of the disperse dye/hydrophobic fibre system has received much attention [see (11)].

In the case of linear, *Nernst* (aka partition) adsorption isotherms being obtained for the adsorption of disperse dyes on PET and other types of fibre, values of standard affinity for the particular dye/fibre system are calculated using Equation 12 or its equivalent form, 13.

If dye adsorption isotherms correlate with a Langmuir-type adsorption model that assumes dye adsorption occurs via the formation of a monolayer of dye molecules that interact with a fixed number of specific sites within the fibre, then $[D]_f$ will be given by Equation 14, values of which can be substituted in Equation 12.

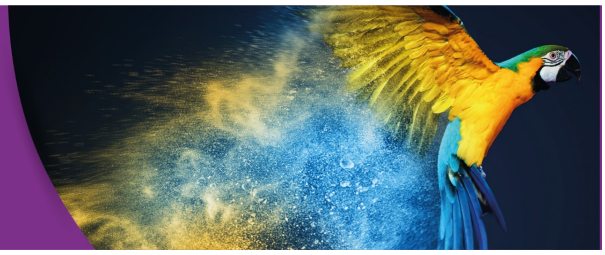
$$[D]_f = \frac{K[D]_s S_f}{1+K[D]_s} \qquad 14$$

Anionic dyes/cotton, CV, CLY fibres

The anionic dye/inorganic electrolyte/cellulosic fibre system has received much attention and several mathematical models have been proposed to interpret equilibrium adsorption data using either Freundlich or Langmuir adsorption models, assuming a Donnan distribution of ions and invoking usage of the concept of fibre internal volume, *V* [see (2, 7, 11, 74)]. For a comprehensive account of this much studied topic see (11).

In essence, the distribution of an anionic dye (eg direct dye, reactive dye) between the dyebath phase and the cellulosic fibre phase in the presence of added inorganic electrolyte (NaCl or Na_2SO_4), under equilibrium conditions, is calculated using a mathematical interpretation of Equation 11, such as Equation 15 (58), which represents the most widely recognised model of the anionic dye/inorganic electrolyte/cellulosic substrate system (as well as the reactive dye/inorganic electrolyte/cellulosic substrate system) (11).

$$-\Delta\mu^o = RT\ln \frac{[Na^+]_f^z [D^-]_f}{V^{z+1}[Na^+]_s^z [D^-]_s} \qquad 15$$



All of the amounts in Equation 15 are measurable except for $[Na^+]_f$, which is calculated (11) using Donnan membrane equilibrium theory utilising the concept of fibre *internal volume*, *V*. In the latter context, considerable debate has attended the nature of the volume term *V*, (11), which was first proposed by Neale *et al* (75) in 1935[1], and subsequently adopted by many workers. Essentially, *V* is ascribed a particular value in equations such as Equation 15, the magnitude of which is considered to be either *unique* for a particular type of cellulosic fibre, irrespective of temperature, pH, electrolyte concentration, etc., or, an *arbitrary value* is given to *V*, in which case, the value of *V* can be varied so as to deliver optimum agreement between experimentally obtained equilibrium adsorption data and a particular thermodynamic model of dye adsorption.

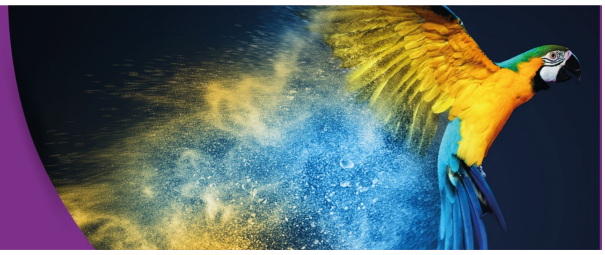
Neale *et al* originally proposed a value of 0.22 l kg^{-1} for *V* in the case of cotton, which represents the amount of water adsorbed by the substrate at 100% *RH*[2], and provided the best fit to equilibrium adsorption data obtained for C.I. Direct Blue on cotton (75). However, as different types of cellulosic fibre possess different *moisture regain*[3] at 100% *RH*, different values of *V* are considered to apply to other types of cellulosic fibre, such CV, lyocell (CLY), etc. [see (2, 11, 74) for a summary]. In essence, models of the anionic dye/inorganic electrolyte /cellulosic fibre system often employ a particular value of *V* for the adsorbing substrate, which the particular researcher considers, will provide the most appropriate values of thermodynamic parameters (standard affinity, standard enthalpy and standard entropy of dyeing). Unfortunately, the facts that the precise nature of the volume term, *V* and the most appropriate value for the parameter have not yet been resolved, leave much to be desired from the viewpoint of the thermodynamic analysis of anionic dye adsorption on cellulosic fibres.

Indeed, such thermodynamic models are fundamentally unable to accurately describe the anionic dye/inorganic electrolyte/cellulosic fibre system, insofar as inconsistencies are observed between calculated dye standard affinity values and equilibrium dye adsorption

[1] in one of a series of quite outstanding papers that concern the mechanism of direct dye adsorption on cellulosic fibres

[2] Relative Humidity (RH) is *a measure of the amount of water vapour (moisture) in air at a given temperature relative to the maximum amount of moisture that the air could hold at that particular temperature. RH is defined as the ratio of the actual vapour pressure to the saturation vapour pressure, over a plane liquid surface at the same temperature, expressed as a %* 76. BSI. BS 1339-1 2002 Humidity: Part 1 Terms, definitions and formulae. 2002.

[3] *moisture regain* (aka *regain*) is *the ratio of the mass of moisture in material to the oven-dry mass. The ratio is usually expressed as a percentage*: 141. Denton MJ, Daniels PN, editors. Textile Terms and Definitions, 11th edition. Manchester: The Textile Institute; 2002.



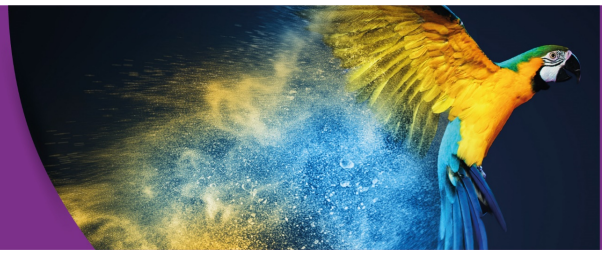
data [see (11)]. The reasons for this are manifold, and include, for example, our somewhat limited understanding of the fine structure of cellulosic fibres (and cellulose polymers in general), especially the accessibility of the -OH groups to both water molecules and dye anions, the role of $-COO^-$ groups in the substrate in dye uptake, and, of relevance to the alkaline application conditions employed for reactive dyes, the effect of $-OH^-$ ions on fibre wetting, fibre swelling, fibre ionisation (dissociation) and fibre plasticisation. From the viewpoint of the anionic dye molecules involved in the dyeing process, our understanding of the nature of aqueous dye solutions, especially those located within the hydrated, swollen, plasticised, cellulosic substrate, remains unclear, as does the precise nature of the effect which inorganic electrolytes have on both dye aggregation and dye solubility. Furthermore, an inherent difficulty when calculating the standard affinity of an anionic dye using equations such as Equation 15 is determining precise values for the concentration of Na^+ ions that reside within the fibre phase [ie $[Na^+]_f$ in Equation 15). This is most conveniently achieved using Donnan membrane equilibrium theory, which invokes the vague and puzzling concept of fibre internal volume, *V*, as well as *electrical double-layer theory* (11) which seeks to describe the ionic environment of a dissolved ion that is in close proximity to a charged surface, such as a cellulosic fibre; none of these particular components of analysis are uncomplicated from either conceptual or mathematical modelling perspectives.

In summary, all thermodynamic models which have been proposed to interpret the anionic dye/inorganic electrolyte/cellulosic fibre system are intrinsically complicated and, also, are conceptually and mathematically challenged, because of the need to employ the incompletely resolved theoretical concept of internal volume in conjunction with a Donnan distribution of Na^+ ions within the fibre phase, in order to account for the effect of added inorganic electrolyte (NaCl or Na_2SO_4) on equilibrium dye uptake.

Anionic dyes/wool, silk and PA fibres, as well as basic dyes/PAN fibres

The first three types of fibre discussed in this section (wool, silk and PA) are considered jointly because they each display chemical and physical resemblances that stem from the presence of both amino groups, $-NH_2$, and carboxyl groups, -COOH, within the component macromolecules; furthermore, similar theoretical approaches are employed to interpret the equilibrium adsorption of anionic dyes on the three types of substrate.

Briefly, several types of anionic dye are used on PA, wool and silk fibres, namely acid dyes (including both non-metallised acid dyes and pre-metallised acid dyes), direct dyes, mordant



dyes and reactive dyes. Whilst the substrates display substantivity towards basic dyes and disperse dyes, as well as vat dyes, sulphur dyes and azoic colorants, these particular five classes of dye enjoy limited, mostly niche usage and are not discussed here. Of the four types of anionic dye under consideration here (ie acid dyes, direct dyes, mordant dyes and reactive dyes), acid dyes, and in particular non-metallised variants, have received greatest attention in the context of the mechanism of adsorption. Furthermore, wool is the most studied type of fibre from a dyeing mechanism viewpoint, with PA fibres running a reasonably close second; in comparison, very few thermodynamic studies of anionic dye adsorption have been carried out on silk and other types of protein fibre.

In this context, it is generally considered that the thermodynamic analysis of the adsorption of non-metallised acid dyes on wool is consonant, to a very large degree, with that on PA fibres and, also, that such analysis applies to silk fibres. Furthermore, to a first approximation, the thermodynamic interpretation of non-metallised acid dye adsorption on wool, silk and PA fibres applies to anionic dyes in general on such fibres and, therefore, can be considered to apply to that of direct dyes, reactive dyes and mordant dyes (prior to complexation with Cr salts) on these substrates.

In order to circumvent the inherent experimental problems involved in determining anionic dye adsorption equilibrium isotherms on wool, the mechanism of adsorption of dye anions on the substrate is modelled on the basis of the adsorption of simple acids (e.g. HCl, H_2SO_4) and alkalis (e.g. NaOH, KOH), in the form of experimentally obtained *titration curves* [e.g. (2, 48-54)] that are of the generic shape displayed in Figure 10.

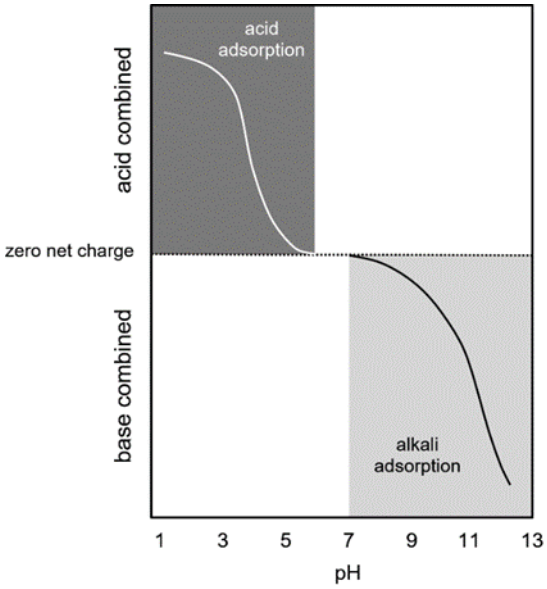


Figure 10 general shape of titration curve obtained for wool and PA fibres with acid and alkali

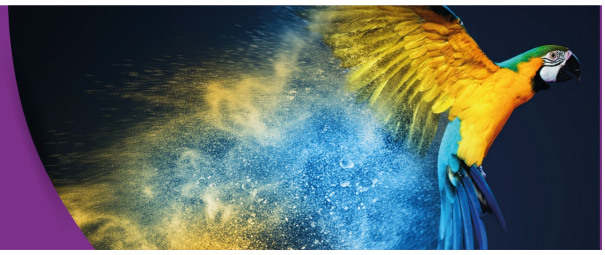
Such titration curves were initially utilised as a means of formulating a model that described anionic dye adsorption on wool[4]. This results in a less than satisfactory situation insofar as the various models that have been proposed to describe the mechanism of anionic dye adsorption on wool are entirely theoretical and have not been adequately corroborated experimentally using data secured in equilibrium dye adsorption isotherms; unfortunately, a similar situation applies in the case of silk and other natural protein fibres, insofar as the mechanism of anionic dye adsorption is assumed to parallel that of wool. Owing to the lower hydrolytic susceptibility of PA fibres, equilibrium dye adsorption isotherms have been obtained for this substrate, as evidenced by the plots shown in Figure 6, although, disappointingly, the (entirely) theoretical models of dye adsorption derived for wool are applied to the synthetic polyamide fibre.

Two approaches have been used to analyse the data obtained from titration curves namely:

(i) a Langmuir-type (*specific site*) model first proposed by Gilbert and Rideal (77);

(ii) various *ion exchange* models that are based on modifications of a Donnan membrane theory originally proposed by Peters and Speakman (78).

[4] even though the titration curves were carried out at temperatures ~≤50°C and under conditions that bear no resemblance to those likely to be encountered in practical wool dyeing (and, of course, did not employ any dyes)



Although such approaches, which were initially devised in the 1940's for modelling dye adsorption on wool, have also been applied to that on PA fibres, a slightly different methodology is utilised for PA fibres because they comprise an excess of carboxyl groups whereas wool contains equal quantities of amino groups and carboxyl groups. Detailed accounts of the principles underlying these two treatments of the titration curves of both protein and PA fibres are available [e.g. (2, 4, 5, 7, 11, 74, 79)].

Essentially, in the case of the adsorption of a simple acid, X^-H^+, the Gilbert-Rideal model assumes that the fibre phase contains the aqueous acid solution in which in which the acid anions, X^-, are adsorbed onto $-NH_3^+$ groups and their associated cations, H^+, are adsorbed onto $-COO^-$ groups within the fibre (Figure 11); thus, it is assumed that the ions are adsorbed according to a Langmuir-type mechanism (ie onto specific sites in the fibre).

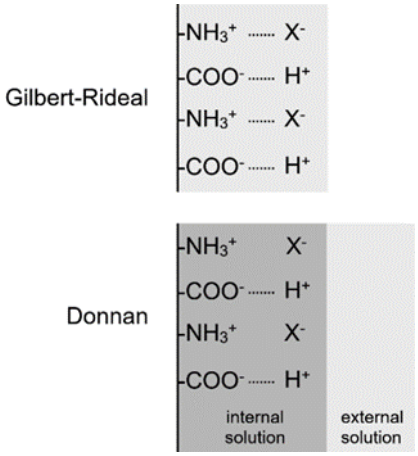
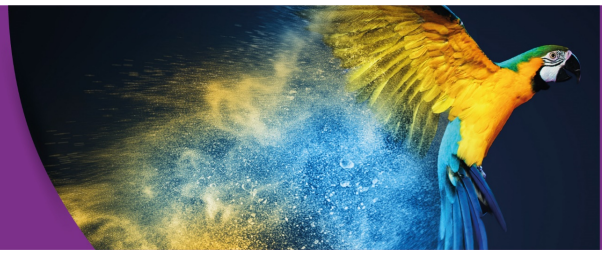


Figure 11 representation of the Gilbert-Rideal and Donnan models of acid adsorption

In contrast, according to the Donnan model (Figure 11), the fibre contains an *internal solution*, of volume, V l kg^{-1} (which invokes the concept of fibre *internal volume*, *V,* that is in equilibrium with an *external (bulk) solution*, a Donnan equilibrium distribution of ions being assumed between the two types of solution. Within the internal solution in the fibre, only cations are adsorbed onto $-COO^-$ group sites; indeed, according to the Donnan model, the acid anions, X^-, do not interact at all with the cationic sites in the substrate but, instead, merely reside within the internal solution (Figure 11). The Donnan model also invokes the concept of the *internal*



pH[5] of the wetted fibre, according to which, the pH within the internal solution is different to that within the external solution (ie bulk dyebath).

Each of these two analyses of acid titration curves enable equations to be derived that can be used to determine the thermodynamic standard affinity, -Δμθ, involved in the adsorption of acids and, by extension, that of acid dyes, on wool , namely Equation 16 in the case of the Gilbert-Rideal analysis, in which θ/(1-θ) represents the activity of the anionic and cationic sites in the fibre, θ the fractional occupation of the sites in the substrate and pH_s the pH of the dyebath phase.

$$\frac{-\Delta\mu^o}{4.606RT} = \frac{\log\ \theta}{1-\theta} + pH_s \qquad 16$$

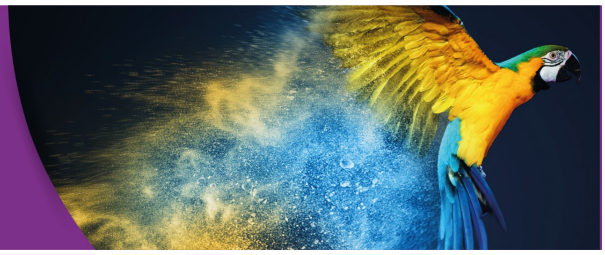
To calculate the standard affinity of a series of acids on wool, the chosen standard condition of θ = 0.5 is commonly used (i.e. at half-saturation of the sites in the substrate) because when θ = 0.5 then (θ/1-θ) = 1 in Equation 16.

$$\frac{-\Delta\mu^o}{2.303RT} - \log\frac{[S]_H}{V} = \log\left(\frac{\theta^2}{1-\theta}\right) + 2pH_s \qquad 17$$

According to the Donnan approach, Equation 17 applies where $[S]_H$ is the maximum amount of anion adsorbed by the substrate, *V* the internal volume of the fibre and pH_s the pH of the external phase (i.e. dyebath).

According to Equation 16, a plot of log θ/(1-θ) versus pH of the dyebath (i.e. pH s) should yield a straight line of negative unit slope (i.e. -1) whilst from Equation 17, a plot of log θ2/(1-θ) versus pH_s should provide a straight line of slope -2. Unfortunately, using acid titration data for wool, a slightly sigmoidal plot of slope -0.88 was secured using Eq 16 (2, 5, 78) and a line of slope -1.4 was obtained using Equation 17 (2). The discrepancies observed between the theoretical predictions of each model and the calculated values interpreted from experimental acid/base titration data can be attributed partly to problems associated with practical difficulties (e.g. fibre hydrolysis, dissolution of oligomeric/monomeric species, dyebath compositional changes, etc.) as well as inherent inadequacies of the two theoretical

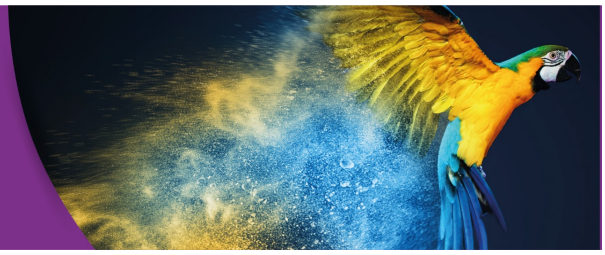
[5] *internal pH* is an entirely theoretical parameter and cannot be measured



approaches that arise from the assumptions upon which the Gilbert-Rideal and Donnan membrane models are based (11, 74).

In the case of PA fibres, because the adsorption of simple acids is considered as being analogous to that on wool, the above theoretical Gilbert and Rideal and Donnan membrane treatments have been applied, in slightly modified form, to account for the non-equivalence of -COOH and -NH2 groups in such substrates [e.g. see (2, 7, 11, 74)]: generally, greater variation in the values of standard affinity of acids adsorbed by PA fibres is displayed by the Donnan model (7, 74). Other mathematical models have been developed to describe acid adsorption within PA fibres [e.g. (78, 80-82)].

In summary, all thermodynamic models which have been proposed to interpret the anionic dye/wool/silk/PA fibre system are inherently complicated, from both conceptual and mathematical viewpoints. Furthermore, the theoretical predictions of both the Gilbert-Rideal and Donnan membrane models do not provide satisfactory correlation with calculated values interpreted from experimental acid/base titration data, which can be partly attributed to over-simplification of the nature and amount of the charged fibre species involved (i.e. -+NH3, -COO-) as well as, in the case of the Donnan membrane approach, the need to employ the incompletely resolved theoretical concept of internal volume in conjunction with a Donnan distribution of charged ions within the fibre phase.



Basic dyes/PAN fibres

The equilibrium adsorption of cationic dyes on PAN fibres accords with a Langmuir isotherm model [e.g. (10, 83-90)], which led Remington and Shroeder (91) in 1957 to propose that the fibre acts as an ion-exchange medium insofar as colourless cations (e.g. Na+, K+, H+) associated with anionic sites (-SO3-; -OSO3-, -COO-) within the fibre, F, are exchanged with dye cations, D+, during dyeing (Figure 16).

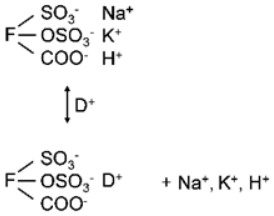


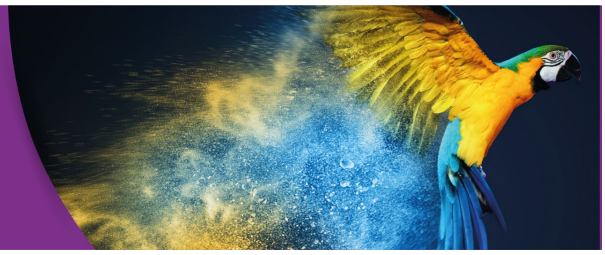
Figure 16 ion-exchange mechanism (11)

This ion-exchange mechanism has been interpreted using two approaches:

(i) A Langmuir adsorption model in which the fibre contains anionic dye sites (e.g. $-SO3^-$, $-OSO_3^-$, $-COO^-$) that are identical in terms of their interactions with adsorbing dye molecules, and the effects of pH and inorganic electrolyte addition on dyeing are considered in totality;

(ii) A Donnan equilibrium model that distinguishes between weakly anionic group (e.g. $-COO^-$) and strongly anionic group ($-SO_3^-$; $-OSO_3^-$) dye sites and considers the influence of all dyebath components (protons, inorganic cations, anions, etc.) separately.

In terms of a Langmuir adsorption model [see (92) for a review of the various approaches], Equation 18 applies where $[D^+]_f$ is the amount of dye cations in the fibre, $[D^+]_s$ and $[H^+]_s$ being the corresponding amounts of dye cations and protons, respectively, in solution, and $[S]_f$ represents the number of available anionic sites in the fibre. For simplicity, activity coefficients are assumed equal to unity in both the fibre and solution phases.



$$\frac{[D^+]_f}{[D^+]_s} = \frac{K_H^D}{[H^+]_s}\left([S]_f - [D^+]_f\right) \qquad 18$$

However, Harwood et al (90) found that Equation 18 provided plots that were linear for only ~80% of the dye concentration range employed and displayed curvature at high dye concentrations, which led to the proposal that dyeing involved two types of anionic group in the film, namely sulfonate, $-SO_3^-$, and sulfate, $-OSO_3^-$, groups.