EQUILIBRIUM CONSTANTS OF HF, F^-, HF_2^- AND H_2F_2 SPECIES IN FORMIC ACID.

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SUMMARY

        Equilibrium constants for the fluorinated species HF, F^-, HF_2^- and
H_2F_2 in formic acid and in a 1M potassium formate solution in formic acid
have been studied by ^{19}F NMR. The chemical shifts of these species have
been determined from measurements of the shifts for various initial mixtures
of differing concentrations of dissolved HF, F^- and HF_2^-. From these values,
relative concentrations of HF, F^-, HF_2^- and H_2F_2 in each solution have been
calculated through a numerical method. The following constants were ob-
tained : $K_1 = [H^+][F^-]/[HF] = 1.1 \times 10^{-5} M$; $K_D = [HF][F^-]/[HF_2^-] = 0.5 M$;

$K_1' = [H^+][HF_2^-]/[H_2F_2] = 1.1 \times 10^{-5} M$; $K_D' = [HF]^2/[H_2F_2] = 0.5 M$.

INTRODUCTION

        In a previous paper [1], a pH scale in pure formic acid was esta-
blished by potentiometric and spectrophotometric methods and the equili-
brium constants K_A of several acids were also measured. The methods used
were inadequate for the determination of the equilibrium constants of hydro-
fluoric acid and potassium bifluoride, because the glass vessels were at-
tacked by the hydrofluoric acid. The dissociation constants of hydro-
fluoric acid and of potassium bifluoride in water have been obtained by an
indirect determination [2]; other determinations of these constants as well

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as determinations of fluorine chemical shifts in water and deuterated water
have been accomplished using ^{19}F nuclear magnetic resonance [3] [4]. In
the present work, we have also been able to use ^{19}F NMR to determine the
equilibrium constants involving the aforementioned species in formic acid.

EXPERIMENTAL RESULTS

Media and solutions studied

Two media were used : pure formic acid (neutral non buffered medium)
I, and formic acid with 1M potassium formate (basic medium) II. Solutions
of hydrofluoric acid HF, potassium fluoride KF, or potassium bifluoride
KHF_2, were made in these media : solutions 1 : HF in I; solutions 2 : KF in
II; solutions 3 : KF in I; solutions 4 : HF in II; solutions 5 : KHF_2 in I;
solutions 6 : KHF_2 in II; solutions 7 : KF and KHF_2 in I. We call C the
initial concentration of the dilute species. In each solution, the four
fluorinated species : H_2F_2, HF_2^-, HF and F^- are present and their relative
concentrations depend on the pH of the medium which depends itself on the
autoprotolysis constant of the solvent K_S [1] and on the equilibrium cons-
tants defined below with the approximation that the activity coefficients
are included in the constants.

$$H^+, F^-, HF \quad \xrightleftharpoons{K_1} \quad HF, HF$$

$$K_D \big\updownarrow\big\updownarrow \qquad\qquad\qquad \big\updownarrow\big\updownarrow K'_D$$
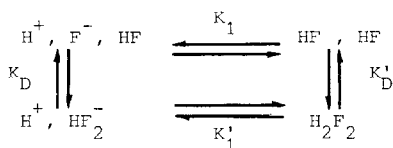
$$H^+, HF_2^- \quad \xrightleftharpoons{K'_1} \quad H_2F_2$$

with $K_1 = \dfrac{[H^+][F^-]}{[HF]}$, $K_D = \dfrac{[F^-][HF]}{[HF_2^-]}$, $K'_1 = \dfrac{[H^+][HF_2^-]}{[H_2F_2]}$, $K'_D = \dfrac{[HF]^2}{[H_2F_2]}$

These constants are related by the equation $K_1 K'_D = K'_1 K_D$. For each solu-
tion the concentrations of all the fluorinated species can be calculated
from the autoprotolysis and equilibrium constants and conservation equations
for mass and charge. The equations are collected in the appendix.

Use of the ^{19}F NMR

The observed chemical shifts are the weighted average of the chemical
shifts of each species present in the medium according to the formula
$\delta(obs) = \sum_i x(i)\delta(i)$ where $x(i)$ is the molar ratio of the species i and $\delta(i)$
its chemical shift, the average resulting from rapid exchange of the four

species. The plot of the observed chemical shift versus the total concen-
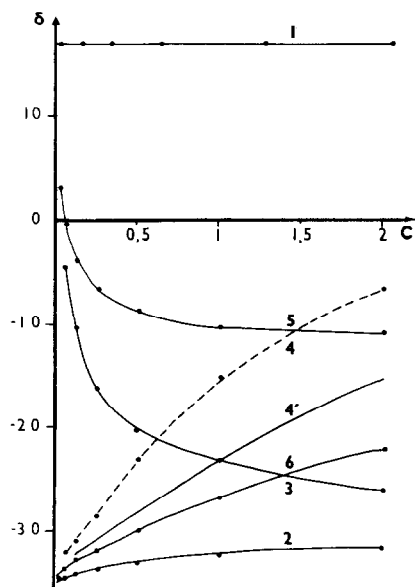tration for solutions 1 to 6 is shown on figure 1.

Fig. 1. Plot of the ^{19}F chemical shift δ (ppm versus C_6F_6) versus
the total concentration C (mole/l) of the fluorinated species for solutions
1 to 6 .

Determination of the chemical shifts

The extrapolation of all plots to infinite dilution gives for medium
I the value + 17 ppm and for medium II the value -34,6 ppm. The plot for
solutions 1 shows no variation of the chemical shift for concentrations of
HF from 2M to 0.06 M . Assuming for the moment, that HF is weakly disso-
ciated and is the predominant species we assume δ(HF) = 17 ppm. At high
concentrations the dimer H_2F_2 can exist but because no variation is shown,
we also assume δ(H_2F_2) = δ(HF). In the same way, from the plot for so-
lutions 2, we assume δ(F^-) = -34,6 ppm. Such an extrapolation is valid if
the species of interest predominates in the medium and if other components
can be neglected. Therefore, a correction of these initial values will
have to be made later on.

Experimental conditions to measure directly the chemical shift of HF_2^- are not available. An approximate value is given by the average of the values of the two dissociated species of the complex $((\delta(F^-) + \delta(HF))/2 = -8$ ppm). However we have prefered to determine this value by numerical adjustment together with the equilibrium constants.

DETERMINATION OF EQUILIBRIUM CONSTANTS BY NUMERICAL ADJUSTMENT.

Four unknown quantities (the three equilibrium constants K_1, K_D, K_1' and the chemical shift $\delta(HF_2^-)$ must be assigned to fit all the experimental data reported in figure 1. The most general numerical adjustment would consist of considering the four unknown quantities as parameters. The calculation can then be carried out in two steps : firstly, using the equations of the media (appendix), the three equilibrium constants being parameters, we should obtain the concentrations of the four fluorinated species in solution and secondly, using the equation $\delta = \sum_i x(i)\delta(i)$, $\delta(HF_2^-)$ being a parameter, we should obtain calculated chemical shifts. This method would be too long and therefore we have adopted a simplifying step procedure that takes into account that in some solutions one or two species could be neglected.

Determination of acidity constant of HF : K_1

For solutions 3, we assumed that for KF concentrations such as $0.06\ M \leqslant C \leqslant 0.5\ M$, only HF and F^- concentrations are not negligible. The system can then be described with only K_1 as an unknown quantity. From the observed chemical shift, HF and F^- concentrations are calculated and we deduce K_1 at each experimental point. The average value is $K_1 = 1.3 \times 10^{-5}$ M. This means that at infinite dilution in the basic medium II the ratio $[F^-]/[HF]$ approaches the limiting value $K_1/K_s = 20.6$. Therefore, for solutions 2, F^- is the preponderant species as assumed when $\delta(F^-)$ was determined, but the HF concentration is not completely negligible. Taking this into account, a corrected value for $\delta(F^-)$ can be calculated by means of the formula $\delta(F^-) = (21.6\ \delta(\lim) - \delta(HF))/20.6$ where $\delta(\lim)$ is the graphically extrapolated value. We obtain $\delta(F^-) = -37$ ppm. This value will be subsequently used. The resulting values of K_1 are given in table 1. For concentrations of KF from 0.062 M to 0.5 M, $K_1 = 1.1 \times 10^{-5}$ M. For higher concentrations of KF, the K_1 values deviate : activity coefficients and other fluorinated species HF_2^- and H_2F_2 are no longer negligible.

TABLE I

Calculation of constant $K_1 = [H^+][F^-]/[HF]$ from data of solutions 3.

C(M)	0.062	0.125	0.25	0.50	1.0	2.0
δ(obs) (ppm)	-5.0	-10.25	-16.25	-20.25	-23.1	-25.75
[HF]	0.037	0.067	0.096	0.155	0.257	0.417
[F$^-$]	0.025	0.061	0.154	0.345	0.743	1.58
$10^5 \times$ [H$^+$]	1.72	1.02	0.66	0.41	0.24	0.15
$10^5 \times K_1$	1.18	1.04	1.05	0.90	0.71	0.57
pK$_1$	4.93	4.98	4.97	5.04	5.15	5.14

$[HF] = C \ (\delta(obs) - \delta(F^-))/(\delta(HF) - \delta(F^-))$; $[F^-] = C - [HF]$; $10^5 \times [H^+] =$
$10^5 \times (-[HF] + ([HF]^2 + 4 \ K_s)^{1/2})/2$; $10^5 \times K_1 = 10^5 \times ([F^-][H^+])/[HF]$;
$pK_1 = -\log(K_1)$.

Determination of the dissociation constant of HF$_2^-$: K_D and of its chemical shift : δ(HF$_2^-$).

In the basic medium II (solutions 2,4,6) for small concentrations of the added species, the F$^-$ concentration is large and the HF concentration is small. For higher total concentrations, HF$_2^-$ ion is present but the dimeric acid H$_2$F$_2$ is always negligible. In the neutral medium I (solutions 3,5) it is assumed that H$_2$F$_2$ concentration is also negligible, but this assumption will have to be verified or corrected later. For these five solutions HF and F$^-$ concentrations at equilibrium are given by fourth order equations whose coefficients depend on K_s, K_1, K_D and C (Appendix, table A2) By numerical solution of these equations by computer, varying K_D as a parameter from 0.01 to 10 M, HF, F$^-$ and HF$_2^-$ concentrations are calculated. Average chemical shifts are then calculated for the five solutions, varying δ(HF$_2^-$) as a parameter from -7 to -20 ppm. Several pairs of the parameters (K_D, δ(HF$_2^-$)) fit the calculated to the experimental values for each point in each solution. We illustrate the dependence between these parameters by the plot of δ(HF$_2^-$) versus log (K_D) (see fig.2). If there is a unique intersection it will provide the values for the two parameters that fit all the experimental data.
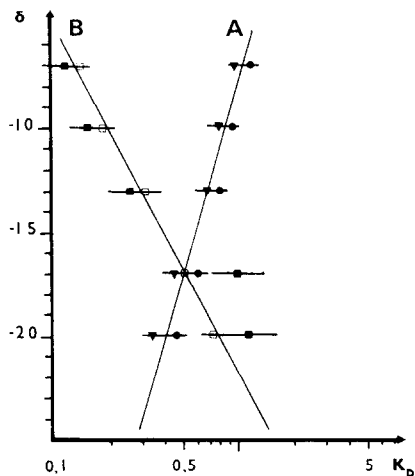
Fig. 2. Plot of possible values of $\delta(HF_2^-)$ versus $\log(K_D)$ showing the dependences between these parameters for solutions 2 and 6 (A) and for solutions 3 (B). Solutions 2 : ●, solutions 3 : ☐, solutions 5 : ■, solutions 6 : ▼.

Results

In a first approximation there is not single crossing point for the five curves. Taking into account the incertitude of the method, the plots for solutions 2 and 6 have the same linear dependence (fig. 2, plot A) solutions 3 also give a linear plot (fig. 2, plot B), with an intersection at $K_D = 0.5$ M ; $\delta(HF_2^-) = -17$ ppm.

The correlations for solutions 4 (not pictured in figure 2) and for solutions 5 do not converge on this point ; for solutions 4, it probably results from errors in the concentrations of anhydrous hydrofluoric acid in formic acid (see experimental); for solutions 5, the observed shift is perhaps related to the non negligibility of the acid H_2F_2, and in this case, the above approximation is not correct. Consequently, we selected the value corresponding to the intersection of plots A and B in figure 2.

Determination of the acidity constant of H_2F_2 : K_1' and of its dissociation constant : K_D'

The preceeding treatment suggests that informations concerning the acid H_2F_2 can be obtained from solutions 5. However, we have studied

solutions 3,4,5 and 6 without using approximations for the four fluorinated species. In this case, the concentrations of a species is obtained by a sixth order equation dependent on K_s, K_1, K_D, C and K_D' where K_D' is the only parameter to be determined (see Appendix, table A3). From K_D' varying from 0.01 to 10 M, we computed the concentration of HF, then the concentrations of other species; we calculated the corresponding chemical shifts for comparison with the experimental values. The best agreement is obtained for K_D' = 0.5 M. Deduced from the other constants K_1' = 1.1 x 10^{-5} M.

COMBINATION AND REEVALUATION OF ALL NMR DATA

The final determination of the chemical shifts of all the solutions is made using on one hand, the sixth order equations with numerical coefficients K_D, K_1, K_D', K_1' previously determined and on the other hand, the chemical shifts of the four fluorinated species in formic acid also previously determined. In table 2, the comparison of calculated and experimental values can be easily made. The agreement is satisfactory for all solutions including the KF-KHF$_2$ solutions in medium I (solutions 7).

Our method of calculation is based on numerically adjusting the calculated values to the experimental ones and does not allow the direct evaluation of standard deviations. Reevaluation of all of the experimental data (34 values without plot 4) leads to mean error below 0.6 ppm. This value provides a measure of absolute error of the method. The error made on equilibrium constants can be approximately deduced by assuming that the experimental chemical shifts also are subject to 0.3 ppm of error and that the relative error of the concentrations is 2%. Thus we have found 25% for the relative error on K_1 that is K_1 = (1.1 ± 0.3)x10^{-5} M. Corresponding pK values are 4.8_5 ⩽ pK_1⩽ 5.1 with the same order of precision as those previously established by potentiometry in formic acid [1].

CONCLUSION

The analysis of the plot of the ^{19}F chemical shifts of solutions of HF, KF and KHF$_2$ in pure formic acid or in basic formic acid (with HCOOK 1 M) versus the total concentration allows the determination of the chemical shifts of the four fluorinated species F$^-$, HF, HF$_2^-$ and H$_2$F$_2$ and of the equilibrium constants for these species. This work does not take into

TABLE 2

Comparison of calculated with experimental values of chemical shifts of ^{19}F with $K_1 = 1.1 \times 10^{-5}$ M ; $K_D = 0.5$ M ; $K_1' = 1.1 \times 10^{-5}$ M ; $K_D' = 0.5$ M.

δ for Solutions C		0.031	0.062	0.125	0.25	0.50	1.0	2.0
1	calc.	16.4	16.5	16.6	16.7	16.8	16.8	16.9
*	obs.	16.9	16.9	16.9	17.1	17.1	17.1	17.1
2	calc.	-34.1	-34.0	-33.8	-33.4	-32.7	-31.8	-30.8
	obs.	-34.5	-34.5	-34.0	-33.7	-33.1	-32.2	-31.2
3	calc.	2.1	-3.8	-9.9	-15.3	-19.7	-23.1	-25.1
	obs.		-5.0	-10.2	-16.2	-20.2	-23.1	-25.7
4	calc.	-34.0	-33.8	-33.3	-32.3	-29.8	-22.8	-9.9
**	obs.			-32.2	-31.0	-28.5	-23.0	-15.0
5	calc.	5.0	1.1	-2.5	-5.5	-8.0	-9.9	-11.4
***	obs.	3.3	-0.5	-3.8	-6.6	-8.7	-10.0	-10.4
6	calc.	-33.9	-33.6	-32.9	-31.6	-29.2	-25.5	-21.4
	obs.	-34.1	-33.6	-33.0	-31.8	-30.0	-26.6	-21.7

$[KHF_2] + [KF]$		0.5 + 0.5		0.5 + 1.0		0.5 + 1.5	
7	calc.	-17.6		-20.7		-22.5	
	obs.	-16.3		-20.1		-21.8	

* calculated values lie below the experimental ones because we take
  $\delta(HF) = + 17$ ppm, neglecting the F^- concentration at infinite dilution
  (Taking it into account $\delta(HF)$ should be 17.3 ppm).

** experimental values are corrected for a systematic error resulting from
   the dilution of HF in HCOOH by adjusting the point C = 0.5 M of solution
   4 with the point C = 1.M of solutions 3 (identical solutions where δ(obs)
   = $^-$23.1 ppm (it corresponds to δ(obs) x 2) ; these results must be
   considered cautiously and are only given for comparison.

*** experimental values are the average of two data.

account the activity coefficients and it is clear that the proposed values can be used only in the concentration range in which they have been determined. The uniqueness of the solution is not explicitly demonstrated, but the coherence of the results for all the seven solutions makes severe errors unlikely.

EXPERIMENTAL.

Formic acid was purified according to a previously described procedure [1]. Hydrofluoric acid were purchased from "Matheson gas product". Potassium formate and potassium fluoride were purchased from "Prolabo", and potassium bifluoride from "BDH". Each was dried several hours in a drying-oven at 120°C. 2M solutions of potassium bifluoride and fluoride were prepared in polyethylene flasks. Other concentrations were obtained by dilution. Solutions of anhydrous hydrofluoric acid were prepared by bubbling the gas through formic acid. Some difficulties in establishing accurate concentrations were encountered because firstly, some of the formic acid was swept away during bubbling, and secondly, some hydrofluoric acid seemed to be evolved during storage and transfer of the solutions.

^{19}F NMR spectra were recorded on a JEOL C 60 HL spectrometer equipped with a 56.44 MHz probe. A field sweep was used. Hexafluorobenzene at a fixed concentration in formic acid was used as an internal standard. Samples under investigation were placed in a teflon insert (Stohler) within the ordinary 5mm NMR tubes.

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Appendix

Putting down : C initial concentration of dissolved species ; $[H^+] = [HCOOH_2^+]$; $X = [F^-]$; $Y = [HF]$; $Z = [HF_2^-]$; $T = [H_2F_2]$; $K_S = [HCOOH_2^+][HCOO^-]$.

TABLE A1

Solutions	mass conservation	charge neutrality
1	$X + Y + 2Z + 2T = C$	$X + Z + K_S/[H^+] = [H^+]$
2	$X + Y + 2Z + 2T = C$	$X + Z + K_S/[H^+] = [H^+] + C + 1$
3	$X + Y + 2Z + 2T = C$	$X + Z + K_S/[H^+] = [H^+] + C$
4	$X + Y + 2Z + 2T = C$	$X + Z + K_S/[H^+] = [H^+] + 1$
5	$X + Y + 2Z + 2T = 2C$	$X + Z + K_S/[H^+] = [H^+] + C$
6	$X + Y + 2Z + 2T = 2C$	$X + Z + K_S/[H^+] = [H^+] + C + 1$

Mass and charge conservation laws for every solution.

First hypothesis : T is neglected before X, Y, Z. The equations giving X and Y are fourth order equations depending on K_1, K_D, K'_D K_S and C whose coefficients appear in table A2. Z is deduced from mass conservation equation.

TABLE A2

	Solutions 2	Solutions 3	Solutions 4		Solutions 5	Solutions 6
X^4	$4K_S/K_1K_D - 1$	$4K_S/K_1K_D - 1$	$4K_S/K_1K_D - 1$	X^4	$4K_S/K_1K_D - 1$	$4K_S/K_1K_D - 1$
X^3	$4K_S/K_1 + 2 + 2C - K_D$	$4K_S/K_1 + 2C - K_D$	$4K_S/K_1 + 2 - K_D$	X^3	$4K_S/K_1 + 2C - K_D$	$4K_S/K_1 + 2C + 2 - K_D$
X^2	$2CK_D + K_DK_S/K_1 + K_D - (K_1K_D + 2C + C^2)$	$2CK_D + K_SK_D/K_1 - (K_1K_D + C^2)$	$CK_D + K_DK_S/K_1 + C^2 + K_D - (K_1K_D + 2C)$	X^2	$K_DK_S/K_1 - K_1K_D + 3CK_D$	$K_DK_S/K_1 - K_1K_D + K_D + 3CK_D - 4C$
X^1	$2CK_1K_D - CK_D - C^2K_D$	$2CK_1K_D - C^2K_D$	$2CK_1K_D - CK_D$	X^1	$2CK_D(2K_1 - C)$	$2CK_D(2K_1 - 1 - C)$
X^0	$- C^2K_1K_D$	$- C^2K_1K_D$	$- C^2K_1K_D$	X^0	$- 4C^2K_1K_D$	$- 4C^2K_1K_D$
Y^4	$4K_1/K_D - 2$	$4K_1/K_D - 1$	$4K_1/K_D - 1$	Y^4	$4K_1/K_D - 1$	$4K_1/K_D - 1$
Y^3	$4K_1 - K_D - 2$	$4K_1 - K_D$	$4K_1 + 2C - K_D - 2$	Y^3	$4K_1 + 2C - K_D$	$4K_1 - K_D + 2C - 2$
Y^2	$K_1K_D + CK_D + 2C + C^2 - (K_D + K_DK_S/K_1)$	$K_1K_D + CK_D + C^2 - K_DK_S/K_1$	$K_1K_D + 2CK_D + 2C - (K_D + K_DK_S/K_1 + C^2)$	Y^2	$K_1K_D - K_DK_S/K_1 + 3CK_D$	$K_1K_D - K_DK_S/K_1 - K_D + 3CK_D + 4C$
Y^1	$CK_D + 2CK_DK_S/K_1$	$2CK_DK_S/K_1$	$2CK_DK_S/K_1 + K_DC - C^2K_D$	Y^1	$2CK_D(2K_S/K_1 - C)$	$2CK_D(2K_S/K_1 - 1 - C)$
Y^0	$- C^2K_DK_S/K_1$	$- C^2K_DK_S/K_1$	$- C^2K_DK_S/K_1$	Y^0	$- 4C^2K_DK_S/K_1$	$- 4C^2K_DK_S/K_1$

Second hypothesis : no species is neglected.

The equations giving Y are sixth order equations depending on K_1, K_D, K'_D, K_S and C, whose coefficients appear in Table A3, just as the equations used to calculate X, Z, T and $[H^+]$ from Y .

TABLE A3

	Solutions 2	Solutions 3	Solutions 4
Y^6	$4/K'^2_D$	$4/K'^2_D$	$4/K'^2_D$
Y^5	$4(1 + K_D/K'_D)K'_D$	$4(1 + K_D/K'_D)/K'_D$	$4(K_D/K'_D + 1)/K'_D$
Y^4	$1 + 4K_D/K'_D + 4/K'_D + 4K_SK_D/K_1K'^2_D$ $- 4K_1/K_D$	$4K_DK_S/K'^2_D + 4K_D/K'_D + 1 - 4K_1/K_D$	$4K_DK_S/K'^2_DK_1 + 4K_D/K'_D + 1 - 4C/K'_D$ $- 4K_1/K_D + 4/K'_D$
Y^3	$K_D+2 + 2K_D/K'_D + 4K_SK_D/K_1K'_D - 4K_1$ $-2CK_D/K'_D$	$4K_DK_S/K_1K'_D + K_D - 2CK_D/K'_D - 4K_1$	$K_D - 2C - 4K_1 + 2 + 4K_SK_S/K_1K'_D$ $- 4CK_D/K'_D + 2K_D/K'_D$
Y^2	$K_D + K_DK_S/K_1 - 2C - C^2 - CK_D$ $- K_1K_D - 4CK_SK_D/K_1K'_D$	$K_DK_S/K_1 - 4CK_DK_S/K_1K'_D - CK_D$ $- K_1K_D - C^2$	$K_DK_S/K_1 - 2CK_D + C^2 - K_1K_D - 2C$ $+ K_D - 4CK_DK_S/K_1K'_D$
Y^1	$- CK_D - 2CK_DK_S/K_1$	$- 2CK_S/K_1K_D$	$C^2K_D - CK_D - 2CK_DK_S/K_1$
Y^0	$C^2K_DK_S/K_1$	$C^2K_DK_S/K_1$	$C^2K_DK_S/K_1$
X =	$(C - Y - 2Y^2/K'_D)/(1 + 2Y/K_D)$	$(C - Y - 2Y^2/K'_D)/(1 + 2Y/K_D)$	$(C - Y - 2Y^2/K'_D)/(1 + 2Y/K_D)$
Z =	XY/K_D	XY/K_D	XY/K_D
T =	Y^2/K'_D	Y^2/K'_D	Y^2/K'_D
$[H^+]$	K_1Y/X	K_1Y/X	K_1Y/X

	Solutions 5	Solutions 6	:: Solutions 7
Y^6	$4/K'^2_D$	$4/K'^2_D$	$8/K'^2_D$
Y^5	$4(1 + K_D/K'_D)/K'_D$	$4(1 + K_D/K'_D)/K'_D$	$4(1 + K_D/K'_D)/K'_D$
Y^4	$4K_D/K'_D + 1 - 4C/K'_D +$ $4K_DK_S/K_1K'^2_D - 4K_1/K_D$	$1 - 4K_1/K_D + 4K_D/K'_D + 4/K'_D$ $- 4C/K'_D + 4K_DK_S/K_1K'^2_D$	$1 + 4K_1/K_D + 4K_SK_D/K_1K'^2_D -$ $4K_1/K_D - 4(A + B)/K'_D$
Y^3	$K_D - 6CK_D/K'_D - 2C - 4K_1$ $+ 4K_DK_S/K_1K'_D$	$K_D - 2C + 2 - 4K_1 + 2K_D(1 + 2K_S/K_1$ $- 3C)/K'_D$	$K_D + 2(B - A) + 2K_D(B - 2A)/K'_D +$ $4K_SK_D/K_1K'_D - 4K_1$
Y^2	$K_DK_S(1 - 8C/K'_D)/K_1 - 3CK_D - K_1K_D$	$K_D - 4C - 3CK_D + K_SK_D/K_1 - K_1K_D$ $- 8CK_SK_D/K_1K'_D$	$A(A - 2B) + K_D(B - 2A) + K_SK_D/K_1$ $- 2A K_SK_D/K_1K'_D - K_1K_D$
Y^1	$2CK_D(C - 2K_S/K_1)$	$2CK_D(C - 1 - 2K_S/K_1)$	$AK_D(A - B - 2K_S/K_1)$
Y^0	$4C^2K_DK_S/K_1$	$4C^2K_DK_S/K_1$	$A^2K_DK_S/K_1$
X =	$(2C - Y - 2Y^2/K'_D)/(1 + 2Y/K_D)$	$(2C - Y - 2Y^2/K'_D)/(1 + 2Y/K_D)$	
Z =	XY/K_D	XY/K_D	XY/K_D
T =	Y^2/K'_D	Y^2/K'_D	Y^2/K'_D
$[H^+]$	K_1Y/X	K_1Y/X	K_1Y/X

$\because A = X + Y + 2Z + 2T = \begin{cases} 2,5 \\ 2 \\ 1,5 \end{cases}$

$\because B = X + Z + K_S/[H^+] - [H^+] = \begin{cases} 2 \\ 1,5 \\ 1 \end{cases}$