

Better Refined Adsorption Isotherm than BET Equation

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Abstract During studying the heat capacity of metals and brightening more than the original Lena's image, we realize that the temperature increasing term obtained binomial expansion is used in the adsorption increasing term ($g_a \frac{N_n}{N_{n-1} - N_n}$) and we could derive the total adsorption isotherm equation with it. In the first layer the quantization does not occur and from 2nd to n th layer the quantization occurs. So as to get the total adsorption isotherm equation we add the quantized terms of the second to n th layers to the non-quantized term of the first layer. All terms are based on the unit surface sites. Hence the adsorption equations are derived much better than BET equation. The surface area is calculated through the integration of the adsorption isotherm equation from the inflection point to the wanted relative pressure.

Keywords Refined BET, Binomial, Transforming, Adsorption Increasing Term, Surface Area, Inflection Point

1. Introduction

We derived the heat capacity equations of metals and then used consistent step multiplication of the appropriate binomial equations [1]. They are fitted to experimental data well [2]. The heat capacity equation (type V) and the adsorption equation (type II) draw sigmoid (S character) lines all together. And they are symmetry each other. The measurement gas of heat capacity is hydrogen or helium. The adsorption gases are water or nitrogen. The movements of their measurement gases are different. The former is expansion and the later contraction.

The most important term in the derivation of heat capacity equation was the temperature increasing term,

$g_b \frac{N_n}{N_{n-1} - N_n}$. In case of adsorption it becomes

$g_a \frac{N_n}{N_{n-1} - N_n}$ of the same form. Here N_n and N_{n-1}

are the total molecules at the layers of n and $n-1$. Let us put g_a which is unit ($g_a = 1$) in data fitting as the constant.

It is a testing constant. If $g_a \frac{N_n}{N_{n-1} - N_n}$ is transformed

into $\frac{1}{m}$ power of z in every derivation of adsorption such

as $g_a \frac{N_n}{N_{n-1} - N_n} = z^{\frac{1}{m}}$ [3], the more advanced adsorption equation than BET eq. comes out.

2. Statistical Modeling of Adsorption Isotherm

Suppose each level has one binomial equation for excitation and non-excitation. And suppose N_1 molecules are excited on g_m localized sites of the unit surface layer

and $\frac{N_2}{m}, \frac{N_3}{m}, \dots, \frac{N_{n-1}}{m}, \frac{N_n}{m}$ molecules on 2nd to

n th sites of the layers in sequence. Here m means quantization. The first adsorption layer has D_l adsorption energy and, the second to n th layer D_h . Hence the

adsorption probability over the first layer is $P_l = W_l \exp(-D_l / k_K t_a)$ and the non-adsorption probability $1 - W_l \exp(-D_l / k_K t_a)$. In the above W_l is

the adsorption constant of the first adsorption layer. t_a is similar to t_s in heat capacity equation. The adsorption constant, W_l is calculable quantity. It is the expression to

combine the rotation and vibration energy of the adsorbed molecules in the first layer. k_K [2] is similar to k_B (Boltzmann's constant). In the combination calculation of

the first layer N_1 can take the values of from 0 to g_m as variables in sequence. Then the binomial equation of the first layer becomes [1]

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Published online at <http://journal.sapub.org/aac>

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$$W_1(g_m, N_1, m) = (P_l + 1 - P_l)^{g_m} = 1 \cong \sum_{N_1 \leq g_m} \frac{g_m!}{(g_m - N_1)!(N_1)!} P_l^{N_1} (1 - P_l)^{g_m - N_1} \quad (1)$$

Next the adsorption probability of N_2 to N_n layers is $P_h = W_h \exp(-D_h / k_K ts)$ and then the non-adsorption probability $1 - W_h \exp(-D_h / k_K ts)$. The constants of these are the same as those of N_1 layer in the above. The binomial expansion equations for N_2 to N_n layers are

$$\begin{aligned} W_2(N_1, \frac{N_2}{m}) &= (P_h + 1 - P_h)^{N_1} = 1 \cong \sum_{\frac{N_2}{m} \leq N_1} \frac{N_1!}{(N_1 - \frac{N_2}{m})!(\frac{N_2}{m})!} P_h^{\frac{N_2}{m}} (1 - P_h)^{N_1 - \frac{N_2}{m}} \\ &\vdots \\ W_{n-1}(\frac{N_{n-2}}{m}, \frac{N_{n-1}}{m}) &= (P_h + 1 - P_h)^{\frac{N_{n-2}}{m}} = 1 \cong \sum_{\frac{N_{n-1}}{m} \leq \frac{N_{n-2}}{m}} \frac{\frac{N_{n-2}}{m}!}{(\frac{N_{n-2}}{m} - \frac{N_{n-1}}{m})!(\frac{N_{n-1}}{m})!} \times \\ &\quad P_h^{\frac{N_{n-1}}{m}} (1 - P_h)^{\frac{N_{n-2}}{m} - \frac{N_{n-1}}{m}} \\ W_n(\frac{N_{n-1}}{m}, \frac{N_n}{m}) &= (P_h + 1 - P_h)^{\frac{N_{n-1}}{m}} = 1 \cong \sum_{\frac{N_n}{m} \leq \frac{N_{n-1}}{m}} \frac{\frac{N_{n-1}}{m}!}{(\frac{N_{n-1}}{m} - \frac{N_n}{m})!(\frac{N_n}{m})!} \times \\ &\quad P_h^{\frac{N_n}{m}} (1 - P_h)^{\frac{N_{n-1}}{m} - \frac{N_n}{m}} \end{aligned} \quad (2)$$

Let us multiply (1) and (2) side by side. Then for $g_m \geq N_1 \geq \frac{N_2}{m} \bullet \bullet \bullet \geq \frac{N_{n-1}}{m} \geq \frac{N_n}{m}$

$$\begin{aligned} W_{amt}(B, N_1, \frac{N_2}{m}, \bullet \bullet \bullet, \frac{N_{n-1}}{m}, \frac{N_n}{m}) &= W_1 W_2 \bullet \bullet \bullet W_{n-1} W_n \cong 1 \\ &\cong \sum_{\frac{N_n}{m} \leq \frac{N_{n-1}}{m}}^{\frac{N_{n-1}}{m}} \bullet \bullet \bullet \sum_{N_1 \leq g_m}^{\frac{g_m}{m}} \frac{g_m! P_l^{N_1} (1 - P_l)^{g_m - N_1} P_h^{N_n - N_1} (1 - P_h)^{N_1 - \frac{N_n}{m}}}{(B - N_1)!(N_1 - \frac{N_2}{m})! \bullet \bullet \bullet (\frac{N_{n-1}}{m} - \frac{N_n}{m})!(\frac{N_n}{m})!} \\ &= \sum_{\frac{N_n}{m} \leq \frac{N_{n-1}}{m}}^{\frac{N_{n-1}}{m}} \bullet \bullet \bullet \sum_{N_1 \leq g_m}^{\frac{g_m}{m}} W_{amt} \end{aligned} \quad (3)$$

In the above

$$N = N_1 + \frac{N_2}{m} + \bullet \bullet \bullet + \frac{N_{n-1}}{m} + \frac{N_n}{m} \quad (3.1)$$

In Eq. (3) the largest term dominates the equation. So the total differential of Eq. (3) becomes the zero which requires that the coefficients of all terms should be zero. Hence by using Stirling's approximation we solve the equation, W_{at} . The first differential equation of Eq (3) becomes

$$\frac{g_m - N_1}{\beta_{am}} (g_a \frac{N_n}{N_{n-1} - N_n}) = \frac{N_1}{m} - \frac{N_2}{m} \quad (4)$$

In the above equations m is quantization constant. In the reference [4] m value should be corrected as those in the present figure [Fig. 1]. The constants have three parts of $m > 1$, $m = 1$, $m < 1$. As we see in Fig. 1, bonding constant mean quantization. If $m > 1$, bonding occurs in many directions. If $m = 1$ no quantization occur and if $m < 1$, the adsorptions are interrupted in many directions. In Eq. (4)

$$\beta_{am} = \frac{W_h}{W_l} \left\{ \exp \frac{-(D_l - D_h)}{k_K t_a} \right\} \left\{ \frac{1 - W_l \exp \frac{-D_l}{k_K t_a}}{1 - W_h \exp \frac{-D_h}{k_K t_a}} \right\} \quad (4.1)$$

$$g_a = 1 - W_h \exp \left(\frac{-D_h}{k_K t_a} \right) = 1 - \exp \frac{-D_h}{k_K t_a} \text{ for } W_h = 1 \quad (4.2)$$

It is possible that g_a is put as unit.

The next equations are

$$\begin{aligned} (N_1 - \frac{N_2}{m})(g_a \frac{N_n}{N_{n-1} - N_n}) &= \frac{N_2}{m} - \frac{N_3}{m} \\ &\bullet \\ &\bullet \\ &\bullet \\ (\frac{N_{n-3}}{m} - \frac{N_{n-2}}{m})(g_a \frac{N_n}{N_{n-1} - N_n}) &= \frac{N_{n-2}}{m} - \frac{N_{n-1}}{m} \\ (\frac{N_{n-2}}{m} - \frac{N_{n-1}}{m})(g_a \frac{N_n}{N_{n-1} - N_n}) &= \frac{N_{n-1}}{m} - \frac{N_n}{m} \quad n=2,3,4,\dots \end{aligned} \quad (5)$$

In Eqs (4) and (5) let us put $g_a \frac{N_n}{N_{n-1} - N_n} = \frac{1}{z^m}$, then $z = p / p_0$ which is same as Eq. (9) of the reference [5] solved by using the chemical potential

$$\begin{aligned} \frac{g_m - N_1}{\beta_a} z^{\frac{1}{m}} &= N_1 - \frac{N_2}{m} \\ (N_1 - \frac{N_2}{m}) z^{\frac{1}{m}} &= \frac{N_2}{m} - \frac{N_3}{m} \\ &\bullet \\ &\bullet \\ &\bullet \\ (\frac{N_{n-3}}{m} - \frac{N_{n-2}}{m}) z^{\frac{1}{m}} &= \frac{N_{n-2}}{m} - \frac{N_{n-1}}{m} \\ (\frac{N_{n-2}}{m} - \frac{N_{n-1}}{m}) z^{\frac{1}{m}} &= \frac{N_{n-1}}{m} - \frac{N_n}{m} \end{aligned} \quad (6)$$

In Eq. (6) add side by side and rearrange

$$\frac{g_m - N_1}{\beta_a} \left(\frac{z^{\frac{1}{m}} - z^{\frac{n}{m}}}{1 - z^{\frac{1}{m}}} \right) = N_1 - \frac{N_n}{m} \quad (7)$$

In Eq. (6) multiple side by side and rearrange

$$\frac{g_m - N_1}{\beta_a} z^{\frac{n-1}{m}} = \frac{N_{n-1}}{m} - \frac{N_n}{m} \quad (8)$$

We solve Eq. (8) with $g_a \frac{N_n}{N_{n-1} - N_n} = z^{\frac{1}{m}}$ in order to eliminate N_{n-1}

$$\frac{g_m - N_1}{\beta_a} \frac{1}{g_a} z^{\frac{n}{m}} = \frac{N_n}{m} \quad (9)$$

We solve Eq. (7) with Eq. (9) in order to eliminate N_n

$$\frac{N_1}{g_m} = \frac{\frac{z^{\frac{1}{m}} - z^{\frac{n}{m}}}{1 - z^{\frac{1}{m}}} + \frac{z^{\frac{n}{m}}}{g_a}}{\beta_a + \frac{z^{\frac{1}{m}} - z^{\frac{n}{m}}}{1 - z^{\frac{1}{m}}} + \frac{z^{\frac{n}{m}}}{g_a}} \quad (10)$$

Eq. (10) represents the adsorption amount of the first layer. It is Langmuir equation. The quantization values (m) and the numbers of the adsorption layer (n) are influential on the determination of N_1 . All values of the parameters (β_a, g_a, n, m) directly participate in the determination of N_1 and following N . The value of g_a is much influential on the

determination of the last term ($z^{\frac{n}{m}}$). But it does not much increase or decrease of N_1 since it exists in the denominator and nominator. At $m=1$ it becomes

$$\frac{N_1}{g_m} = \frac{\frac{z - z^n}{1 - z} + \frac{z^n}{g_a}}{\beta_a + \frac{z - z^n}{1 - z} + \frac{z^n}{g_a}} \quad (11)$$

Therefore the total adsorption amount per unit surface (g_m), that is, the adsorption isotherm for from first layer to the last (n) layer becomes by using Eqs (6) and (10) as follows

$$\begin{aligned} \frac{N}{mg_m} &= \frac{N_1}{g_m} + \frac{N_2}{mg_m} + \frac{N_3}{mg_m} + \dots + \frac{N_{n-1}}{mg_m} + \frac{N_n}{mg_m} \\ &= \frac{1}{g_m} \left\{ N_1 + \left(\frac{N_2}{m} - \frac{N_3}{m} \right) + 2 \left(\frac{N_3}{m} - \frac{N_4}{m} \right) + \dots + (n-2) \left(\frac{N_{n-1}}{m} - \frac{N_n}{m} \right) + (n-1) \frac{N_n}{m} \right\} \end{aligned} \quad (12)$$

If g_m is eliminated in Eq (12) N becomes as follows

$$N = \frac{a}{\beta_a + a} \left\{ 1 + \frac{1}{a} \left(\frac{z^{\frac{2}{m}} - z^{\frac{n}{m}}}{1 - z^{\frac{1}{m}}} + \frac{n-1}{g_a} z^{\frac{n}{m}} \right) \right\} \quad (12.1)$$

If $g_a = 1$, N is a linear function of four variables.

In the above

$$a = \frac{\frac{1}{z^m} - \frac{n}{z^m}}{\frac{1}{1 - z^m}} + \frac{z^m}{g_a} \quad (12.2)$$

And the total adsorption rate is a linear function of z made of four constants (β_a, g_a, n, m). The equation draws BET-like lines and fits BET type experimental data well. At $m = 1$ it becomes

$$\frac{N}{g_m} = \frac{1}{g_m} (N_1 + N_2 + N_3 + \dots + N_{n-1} + N_n) = \frac{a'}{\beta_a + a'} \left\{ 1 + \frac{1}{a'} \left(\frac{z^2 - z^n}{(1 - z)^2} + \frac{n-1}{g_a} z^n \right) \right\} \quad (13)$$

In the above

$$a' = \frac{z - z^n}{1 - z} + \frac{z^n}{g_a} \quad (13.1)$$

If the measurement gas is nitrogen, the general empirical formulae, $A_m = 1.091 \left(\frac{M}{\rho N} \right)^{\frac{2}{3}} \times 10^{16}$ is introduced into.

$S = \frac{x_m}{M} \times N \times A_m \times 10^{-20}$ to get the specific surface area of the adsorbent, S [6]. Then M is the molecular weight of nitrogen and ρ density of nitrogen and N Avogadro number, Hence from empirical formulae $A_m = \text{\AA}^2/\text{number}$ is used. The monolayer capacity, x_m should also be substituted by the value of the integration of Eq. (12) subtracted by the surface adsorption isotherm (N_1/g_m).

3. Result and Discussion

The base of Eq. (10) and Eq. (12) is $\beta_a + a$. So we may use the word, the rate without the dimensionless analysis. It affects the equation totally. Fig. 2 shows the total adsorption rate according to the values of β_a . In accordance with the values of z approaching units, the total adsorption rates approach closely with one another. This seems to mean that the adsorption heat of the first layer is same as those of $2 \sim n$ layers. We call m the quantization values. It seems to have same notion as the quantization appears in quantum mechanism. We are dealing statistical quantization which should exist in statistics. We can differentiate them, three cases. $m > 1$, $m = 1$ and $m < 1$. The cases of $m > 1$, and $m = 1$ explain bonding and $m < 1$, explains existence of the interruptions for bonding. Fig 3 explains the increase of the adsorption rate according to m values. Less m than unit seem to interrupt the bonding. Fig. 4 represents the total adsorption rates according to n values. At less z than 0.5 the isotherms show the same adsorption rates. The constant g_a showed in Fig 5 should be positive. When $g_a = .5$, the constants draw the type II isotherm. At $g_a = .05$ or $g_a = .005$ the same types of the isotherm appear. g_a can include greater values than or equal unit. $g_a = 1.0$ seems to be best. Fig. 6 shows N_1/g_m with respect to the relative pressure like Langmuir's lines which can't become unit even if a is very large or β_a much smaller. The parameter values of Fig. 2 come from the following Fig. 7 and Fig. 8. According to the above variations we optimized two kinds of the experimental adsorption data showed in Figs. 7 [6] and 8 [7] using trial and error method. The experimental data of Fig. 7 are obtained from the Figure 2-10 of the reference [6]. The experimental data are fitted to Eq. (12) well. As we see in Figs 7 and 8, BET isotherm can't imitate the experimental data except for beginning.

What is the catalyst? As we see Fig. 9 in the above, 1, 2, 3, 4, 5, 6 and 7 molecules can function as the catalyst. That is, the molecules of the surface adsorption layer can't function like the catalyst. Because they use much energy in order to hold the surface. So they are not active. The molecules which lie on the surface layer adsorption molecules which hold the surface, can

function as the real catalyst. Therefore in Eq. (12), $\frac{1}{\beta_a + a} \left\{ \left(\frac{\frac{2}{z^m} - \frac{n}{z^m}}{\frac{1}{(1 - z^m)^2}} + \frac{n-1}{g_a} z^m \right) \right\}$ part must work in the catalytic

reaction. Hence the real adsorption equation becomes

$$\frac{N_{real}}{g_m} = \frac{1}{\beta_a + a} \left\{ \left(\frac{z_m^{\frac{2}{m}} - z_i^{\frac{2}{m}}}{\frac{1}{(1 - z_m^{\frac{1}{m}})^2}} + \frac{n-1}{g_a} z_m^{\frac{n}{m}} \right) \right\} \quad (14)$$

If this equation is integrated from the inflection point (z_i) to each optional relative pressure (p/p_0), we get the mono-area capacity (S_m) with respect to the relative pressure (p/p_0). Tables 1 and 2 include those. Then the surface area for the catalyst obtained from the equation becomes $S(m^2/g) = (S_m/M) \cdot N \cdot A_m \times 10^{-20}$ with $A_m = 16.2 \text{ Å}^2$ per number for nitrogen and $A_m = 0.59 \times 16.2 \text{ Å}^2$ per number for water (Table 2) [6] by substituting x_m in the equation of (2.60) of the reference [6] by $S_m = \int_{z_i}^{z_m} \frac{N_{real}}{g_m} dz$ in which z_i =inflection point and z_m =optional z value after the inflection point. In the above equation M is the molecular weight (g) per g-mole and N Avogadro number per g-mole.

Table 1. S_m (mono-area capacity) and S (surface area) for Fig. 7

p/p ₀ integration interval Inflection point ($z_i = 0.573$)	S_m for Fig.7 ($m=0.9, n=3.28, \beta_a = 0.000011, g_a = 1.0$) $S_m = \int_{z_i}^{z_m} \frac{N_{real}}{g_m} dz$	$S(m^2/g)$ for Fig. 7 = Surface Area of Catalyst, Nitrogen
0.573-0.6	0.000042	0.2927
0.573-0.7	0.000199	1.3869
0.573-0.8	0.000355	2.4741
0.573-0.9	0.000512	3.5683

Table 2. S_m (mono-area capacity) and S (surface area) for Fig. 8

p/p ₀ integration interval Inflection point ($z_i = 0.26$)	S_m for Fig.8 ($m=2.4, n=4.5, \beta_a = 0.12, g_a = 1.0$) $S_m = \int_{z_i}^{z_m} \frac{N_{real}}{g_m} dz$	$S(m^2/g)$ for Fig. 8 = Surface Area of Catalyst, Water
0.26-0.3	0.00175	5.5968
0.26-0.4	0.00615	19.6690
0.26-0.5	0.01050	33.5812
0.26-0.6	0.01490	47.6533
0.26-0.7	0.01930	61.6665
0.26-0.8	0.02372	76.0261
0.26-0.9	0.02810	89.8698

Then the inflection points are obtained by Secant method [8] through the program showed in Appendix 1. Specific surface areas are changed according to the optional relative pressures. These are showed in Tables 1 and 2 precisely. The integrations with respect to z surface values give the total adsorption site numbers of the adsorbate. Before the inflection point the specific surface area of the adsorbent is not counted as a catalyst since it makes the strong surface film [9]. The adsorption rate increases consistently after the inflection point. The values of n of Fig. 7 and Fig. 8 match the range of the reference of BET [10]. The completion of N_1 to unit goes with the completion of N to the end as we see in Fig. 6 and its equation. But from the inflection point the pilling up of N/g_m may begin characteristically.

Eq. (13) can be used in the data fitting with $m = 1.0$ and $g_a = 1.0$. Its quality is poor.

Our study have realized the saying that “After considerable work on the theory, Hill (1946) formed the opinion that any

future improvement on it must be in the form of refinement rather than a modification on the basic theory” [11, 12].

4. Conclusions

The total adsorption rate equations closely related with the past references are derived correctly and the figures according to four constants (m, n, β_a, g_a) are also considered to describe BET-like figures (II) well. The quantization constants are useful in deriving the adsorption equations. In order to calculate the surface area of the catalysts the total adsorption equations excluding the first layer adsorption equation and their inflection points obtained are used appropriately. They fit the experimental data well.

ACKNOWLEDGEMENTS

The author thanks for the challenging encouragements of Yongduk Kim, an emeritus professor of Sogang University. And the author thanks for helping the manuscript arrangement of Jones Cathy (<http://www.sapub.org/>), USA.

Appendix 1

/*--Finding zero by Secant method [8] to get inflection point from Eq. (12). with c++ and c languages */

```
#include<iostream>
using namespace std;
#include<stdio.h>
#include<math.h>
#include<conio.h>
float eval_f(float x);          //evaluation of f(x)
float fprime(float x1,float x2); //diff. of f(a)

void main()
{ float x1,x2,xn,e;
  int i=0;
  printf("\nType initial point: ");
  scanf("%f", &x1);
  printf("\nType second point: ");
  scanf("%f",&x2);
  printf("\nType acceptable error interval in y: ");
  scanf("%f", &e);

  i=0;
  do
  { xn=x1-e*eval_f(x1)/fprime(x1,x2);
    x1=x2;
    x2=xn;
    printf("\n%3dth Iteration Root :%f <with error %f >\n",
          ++i,xn,fabs(eval_f(xn)));
    getch();
  } while(fabs(eval_f(xn))> e);
}

float eval_f(float x)
{ float b;
  //cout<<"x="<<x<<endl;
```

```

double bc;
double bb,bb1,bb2,cc,dd,dd1,dd2,dd3,ee,ee1,ee2,ff,ff1,ff2;
double aa,aa1,aa2,ba1,ba2,ba3,ccc1,ccc2,cc1,cc2,cc3,cc4,cc11,cc12;
const double b1=.000091,ga=.983,an=10.0,am=.64;
double ad21,ad22,ad23;
bb=pow(x,(1./am))-pow(x,(an/am));
bb1=(1./am)*pow(x,(1./am)-1.)-(an/am)*pow(x,(an/am-1.));
bb2=(1./am)*(1./am-1.)*pow(x,(1./am)-2.)-(an/am)*(an/am-1.)*pow(x,(an/am-2.));
ccc1=-(1./am)*pow(x,(1./am)-1.);
ccc2=-(1./am)*(1./am-1.)*pow(x,(1./am)-2.);
cc1=pow((1.-pow(x,(1./am))),-1.);
cc2=pow((1.-pow(x,(1./am))),-2.);
cc3=pow((1.-pow(x,(1./am))),-3.);
cc4=pow((1.-pow(x,(1./am))),-4.);
dd=pow(x,(an/am))/ga;
dd1=(an/am)*pow(x,((an/am)-1.))/ga;
dd2=(an/am)*(an/am-1.)*pow(x,((an/am)-2.))/ga;
ee=pow(x,(2./am))-pow(x,(an/am));
ee1=(2./am)*pow(x,(2./am)-1.)-(an/am)*pow(x,(an/am)-1.);
ee2=((2./am)*(2./am-1.)*pow(x,(2./am)-2.)-(an/am)*(an/am-1.)*pow(x,(an/am-2.));
ff=((an-1.)/ga)*pow(x,(an/am));
ff1=((an-1.)/ga)*(an/am)*pow(x,(an/am)-1.);
ff2=((an-1.)/ga)*(an/am)*(an/am-1.)*pow(x,(an/am)-2.);

aa=bb*cc1+dd;
aa1=bb1*cc1+(-1)*cc2*ccc1*bb+dd1
aa2=bb2*cc1+(-1)*cc2*ccc1*bb1+(-1)*(-2)*cc3*ccc1*ccc1*bb+(-1)*ccc2*cc2*bb+(-1)*bb1*cc2*ccc1+dd2;

ba1=pow((b1+aa),-1);
ba2=pow((b1+aa),-2);
ba3=pow((b1+aa),-3);

ad21=aa2*ba1+(-1)*ba2*aa1*aa1+(-1)*(-2)*ba3*aa1*aa1*aa+(-1)*aa2*ba2*aa+(-1)*aa1*aa1*ba2;

ad22=ee2*cc2*ba1+(-2)*cc3*ccc1*ee1*ba1+(-1)*ba2*aa1*ee*cc2+(-2)*(-3)*cc4*ccc1*ccc1*ee*ba1+(-2)*ccc2*cc2*ee*ba1+(-2)*ee1*cc3*ccc1*ba1+(-2)*(-1)*ba2*aa1*cc3*ccc1*ee+(-1)*(-2)*ba3*aa1*aa1*ee*cc2+(-1)*aa2*ba2*ee*cc2+(-1)*ee1*ba2*aa1*cc2+(-1)*(-2)*cc3*ccc1*ba2*aa1*ee1;

ad23=ff2*ba1+(-1)*ba2*aa1*ff1+(-1)*(-2)*ba3*aa1*aa1*ff+(-1)*aa2*ff*ba2+(-1)*ff1*ba2*aa1;
b=ad21+ad22+ad23;
return(b);
}
float fprime (float x1,float x2)
{ float b6;
b6=(eval_f(x2)-eval_f(x1))/(x2-x1);
return(b6);
}

```

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