CALCULATION OF THE COMPOSITION OF BINARY AZEOTROPIC MIXTURES AS A FUNCTION OF PRESSURE AND TEMPERATURE

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An analytical method has been devised for calculating the composition of an azeotropic mixture at one temperature or pressure from the known composition at another pressure and temperature. The calculation is based on the following property of binary azeotropes: at a temperature such that the vapour pressure of the components are equal, $p_1 = p_2$, the composition of the azeotrope becomes equimolar[1,2]. This rule holds well in many systems, particularly in those in which the deviation from ideality is fairly symmetrical. Thus the determination of the second point on the straight line reduces to finding the point of intersection of the vapour pressure–temperature curves of the components. A general formula for the calculation of the composition may be found as follows. Let components A and B form an azeotropic mixture the composition of which is known only at pressure p_1, and let the content of component A be n_1 wt.% at this pressure.

Let p_0 be the pressure at which the boiling points of components A and B are equal. According to the above, the content of component A is 50 mole % or n_0 wt.%. From the linear relation between the composition of the azeotropic mixture and the logarithm of the pressure, we have

$$\frac{\Delta \log p}{\Delta n} = \frac{\log p_1 - \log p_0}{n_1 - n_0}, \quad (1)$$

where $\Delta \log p$ is the change in the logarithm of the pressure from $\log p_1$ to $\log p_2$, p_2 being the desired pressure, and Δn is the change in the concentration of component A, in wt.%, from the initial value n_1.

Eqn. (1) may be rearranged to give

$$\frac{\log p_2 - \log p_1}{n_2 - n_1} = \frac{\log p_1 - \log p_0}{n_1 - n_0}. \quad (2)$$

Consequently the concentration of component A in the azeotropic mixture at pressure p_2 is given by

$$n_2 = n_1 + \frac{\log p_2 - \log p_1}{\log p_1 - \log p_0}(n_1 - n_0), \quad (3)$$

where n_2 is the concentration, in wt.%, of component A in the azeotropic mixture at pressure p_2.

An equivalent formula, for the calculation of the composition of the azeotropic mixture when the temperature of the equilibrium phases is altered, may be derived analogously:

$$m_2 = m_1 + \frac{T_2 - T_1}{T_1 - T_0}(m_1 - 50), \quad (4)$$

where T_0 is the temperature at which $p_1 = p_2$, T_1 is the temperature at which the composition of the azeotropic mixture is known, and m_1 and m_2 are the concentrations (mole %) of one of the components at temperature T_1 and at the required temperature T_2 respectively (the temperatures are in °C).

As an example, a calculation for a benzene + cyclohexane mixture is given below. According to Storonkin and Morachevskii[3] the concentration of cyclohexane in an azeotropic mixture with benzene at 760 mm Hg is 48.1 wt.%. According to Stull[4], the boiling points of benzene and cyclohexane are equal at a pressure of 200 mm Hg. In an equimolar mixture the concentration of cyclohexane is 51.9 wt.%. Let us determine the composition of the azeotrope at a pressure of 495 mm Hg. On substituting the initial data in formula (4), we obtain the concentration of cyclohexane in the azeotropic mixture equal to 49.1 wt.%, corresponding to 47.3 mole %, whereas according to Storonkin and Morachevskii's experimental data the concentration of cyclohexane in the azeotrope at this pressure is 47.4 mole %.

Another example: According to Sheinker and Peresleni[5] the formic acid–water azeotropic mixture contains 43 mole % of formic acid at 42.3°. The vapour pressures of formic acid and water become equal at 95°. Let us determine the concentration of formic acid in the azeotrope at 56°. On substituting the initial data in formula (4), we obtain the concentration of formic acid in the azeotrope equal to 45 mole %. The experimental concentration of formic acid in the azeotrope[5] at 55.9° is 46 mole %.

The above examples show that the proposed method for the calculation of the composition of azeotropic mixtures following pressure and temperature changes is fully satisfactory. The data necessary for such calculations are available for most azeotropic mixtures. The accuracy of the result obtained will be higher, the greater the difference between the pressure (temperature) at which the components of the azeotropic mixture have the same boiling point (equal vapour pressures) and the pressure (temperature) at which the composition of the azeotrope is known.

SUMMARY

An analytical method has been proposed for the calculation of the composition of an azeotropic mixture at any temperature and pressure from the known composition at one temperature and pressure and the temperature dependence of the vapour pressures of the pure components.

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ANODIC BEHAVIOUR OF IRON IN THE PRESENCE OF ANIONS IN ALKALINE SOLUTION

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The effect of foreign ions, *e.g.* Cl^-, SO_4^{2-}, on the anodic behaviour of iron in alkaline solutions is of considerable practical and theoretical interest. The activating action of chloride ions on the corrosion of iron is explained either

by the specific adsorption of the anions changing the structure of the adsorbed layer on the electrode surface and retarding further adsorption of oxygen[1], or by the fact that dissolution of the protective oxide film is facilitated in the presence of Cl^-, or that these films are permeable to chloride ions.

The explanation obviously depends on the view held as to the mechanism of the passivating action of oxygen. Several investigators[2-4] consider that the passivation of iron in alkali is an adsorption process. Some[5] regard the passivity of iron in alkaline solutions as being due to the formation of an extremely thin, non-porous, difficultly soluble chemisorbed layer, with electronic conduction. The quantity of oxygen sufficient for stable passivation appears to be less than that necessary to cover the surface of the iron with an adsorbed layer one atom thick, although under appropriate conditions the surface may be covered with a continuous monatomic passivating layer, which may then actually increase to a diatomic and a triatomic layer. However, such a thin film may also be regarded as adsorbed.

In the presence of chloride ions in alkali the anodic dissolution of active iron leads at first to the formation of ferrous and then of ferric hydroxide, just as in alkali alone. But on further anodic polarisation, the potential passes through a maximum, and then becomes steady at a value even higher than the equilibrium potential for the conversion of ferrous into ferric iron. During this period there is a very protracted oxidation of iron to ferrous hydroxide localised on a small fraction of the surface. The first stage of this reaction occurs by the same mechanism as in acid solutions[1]:

$$Fe \rightarrow Fe^{2+} \rightarrow Fe(OH)_2.$$

Other workers[6,7] have also observed the local corrosion of iron in the presence of Cl^- ions in acid and faintly alkaline solutions.

Lepin' *et al.*[8] studied the dependence of the rate of iron corrosion on the initial pH value in solutions of KOH alone and in the presence of 0.1–1.0 *N* KCl. In the alkali solutions containing added KCl the initial pH necessary for complete suppression of the corrosion of iron (pH 14) was about one unit higher than in the pure alkali solution (pH 13).

Hackerman and Stephens[9] established the specific adsorption of SO_4^{2-} ions on iron and their partial desorption on the introduction of large quantities of Cl^-, and Balashova[10] found a specific adsorption of SO_4^{2-} on platinum. Rozenfel'd[11] observed the passivating action of the SO_4^{2-} ion on steel in neutral solutions of NaCl + Na_2SO_4, but no such effect was observed on iron. Furthermore, introduction of sulphate into the electrolyte facilitated the anodic dissolution of the iron.

The purpose of the present work was to clarify the conditions under which the dissolution of iron in hot alkaline solutions can be strongly activated in the presence of Cl^-, SO_4^{2-}, and other ions, and to determine the mechanism of the action of these anions.

EXPERIMENTAL

Anodic charging and polarisation curves were obtained in NaOH solutions over the concentration range 0.001–10 *N* with various concentrations of Cl^- and SO_4^{2-}. The test electrodes were made of standard spectroscopic iron wire. Measurements were made at 90° in a glass cell provided with a water jacket[12]. The electrode potentials were measured by a null method against a mercury oxide electrode with the same alkali concentration and at the same temperature as the main cell. The auxiliary electrode for polarisation was a platinum wire separated from the main solution in the cell by a glass sinter.

All experiments were carried out in an atmosphere of purified nitrogen and with solutions of alkali which had been carefully purified by polarisation and salts which had been recrystallised twice.

RESULTS

In concentrated solutions of alkali, as can be seen from the anodic polarisation curves in Fig. 1, low concentrations of Cl^-, SO_4^{2-}, and CO_3^{2-} ions have only a slight effect on the anodic behaviour of an iron electrode. In the presence of Cl^- and CO_3^{2-} ions and in pure alkali a sharp increase in potential to 0.6–0.7 V (with respect to the mercury oxide electrode), characteristic of complete passivation of the iron anode and the start of oxygen evolution, is observed at a current density slightly above 10^{-3} A cm^{-2}. At lower current densities anodic oxidation of the iron occurs. In the presence of SO_4^{2-} ions an additional step is observed on the curves (see below).

In the case of metals of variable valency, in particular iron, incomplete passivation can be observed, when oxygen evolution is accompanied by the dissolution of iron with formation of the ferrate (FeO_4^{2-}) ion. It was found analytically that, in 8 *N* NaOH + 0.01 *N* NaCl with an anodic current density of 0.05 A cm^{-2} applied for several hours, the evolution of oxygen is accompanied by the formation of ferrate at an initial rate of 0.1 mg of iron dissolved per hour per square centimetre of surface of the iron electrode; the rate of formation of ferrate gradually falls.

The effect of chloride ions on the rate of corrosion of iron to form $Fe(OH)_2$ was examined at low alkali concentrations. Fig. 2 shows anodic polarisation curves obtained in 2 *N* NaCl solutions with alkali concentrations 0.001–2.0 *N*. In a solution of 2 *N* NaOH + 2 *N* NaCl (Fig. 2, curve *6*) the passivation of the iron electrode is the same as that typical

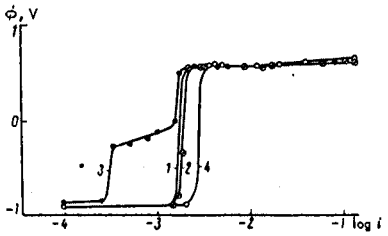

Fig. 1. Anodic polarisation curves obtained at an iron electrode in solutions of 10*N* NaOH containing the following salts:
1) no additive; 2) + 0.01*N* NaCl; 3) + 0.01*N* Na_2SO_4; 4) + 0.01*N* Na_2CO_3.

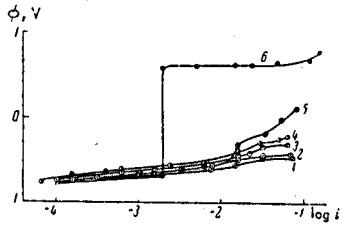

Fig. 2. Anodic polarisation curves obtained at an iron electrode in solutions of 2 *N* NaCl with the following concentrations (*N*) of NaOH: 1) 0.001; 2) 0.01; 3) 0.05; 4) 0.1; 5) 0.5; 6) 2.

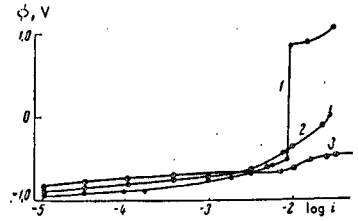

Fig. 3. Anodic polarisation curves obtained at an iron electrode in solutions of 0.05 *N* NaOH with the following concentrations (*N*) of NaCl: 1) 0.01; 2) 0.1; 3) 4.

of concentrated solutions of alkali alone (Fig. 1, curve *1*). In the presence of Cl^- in more dilute solutions of caustic soda (Fig. 2, curves *1–5*) anodic dissolution of iron at potentials between -0.5 and -0.8 V is observed up to a current density of 0.01 A cm^{-2}. At higher current densities the inflection appears on the curves earlier, the greater the concentration of alkali. At all current densities a flocculent greenish deposit of $Fe(OH)_2$ is formed over the whole surface of the electrode. Anodic polarisation curves were also recorded in dilute solutions of caustic soda having different contents of chloride ions. Increase in the chloride ion concentration (see Fig. 3, curves *2* and *3*) leads, at current densities above 0.01 A cm^{-2}, to activation and then to a shift to more negative values of the potential at which dissolution of iron occurs. At lower current densities Cl^- has the opposite effect on the potential.

The action of SO_4^{2-} ions on the anodic dissolution of iron in alkali was examined. The presence of the SO_4^{2-} ion in dilute (0.001–0.01 *N*) solutions of alkali increases the minimum current density for the anodic passivation of iron by a factor greater than 10^3 (Fig. 4). Thus the activating effect of SO_4^{2-} ions is clearly exhibited in dilute solutions of alkali. In concentrated solutions the increase in the minimum passivating current density is smaller (Fig. 5, curves *2* and *4*). A decrease in the alkali concentration by a factor of 10 (in the range of low alkali concentration) in the presence of 1 *N* Na_2SO_4 involves a severalfold increase in the minimum current for complete passivation (Fig. 6, curves *2–4*). At alkali concentrations above 0.5 *N* the opposite effect is observed (Fig. 6, curves *4–6*). With some ratios of alkali to sulphate, the polarisation curves show two steps (Fig. 5, curve *1*; Fig. 1, curve *3*; Fig. 6, curves *3-5*): the first, at potentials of -0.4 and -0.2 V, corresponds to the anodic dissolution of iron with a greater overpotential than in concentrated solutions of alkali alone (Fig. 1, curve *1*); and the second, at potentials of 0.6–0.7 V, corresponds to the passive state of the electrode and the evolution of oxygen. The first step shows the effect of SO_4^{2-} ions in increasing the overpotential, which is to some extent opposed to the activating effect of SO_4^{2-} mentioned above.

The activating action of SO_4^{2-} ions is clearly revealed on the charging curves obtained in 0.01 *N* NaOH + 1 *N* Na_2SO_4 solution at anodic current densities of 0.8, 1.2, and 30 mA cm^{-2}. At all these current densities dissolution of

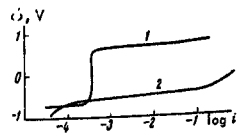

Fig. 4. Anodic polarisation curves obtained at an iron electrode in the following solutions: 1) 0.01 *N* NaOH; 2) 1 *N* Na_2SO_4 + + 0.01 *N* NaOH.

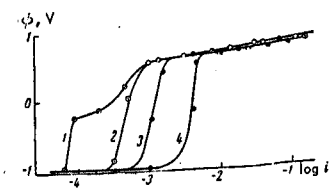

Fig. 5. Anodic polarisation curves obtained at an iron electrode in 5 *N* NaOH solutions with the following concentrations (*N*) of Na_2SO_4: 1) 0.001; 2) 0.1; 3) 0.5; 4) 1.

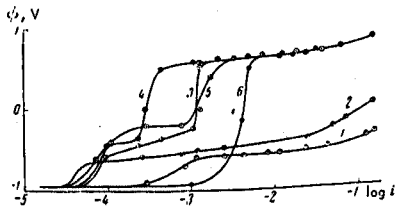

Fig. 6. Anodic polarisation curves obtained at an iron electrode in 1 *N* Na_2SO_4 solutions with the following concentrations (*N*) of NaOH: 1) 0.001; 2) 0.01; 3) 0.1; 4) 0.5; 5) 2; 6) 5.

iron takes place in the presence of the SO_4^{2-} ion for several hours at an almost constant potential without the onset of passivation, whereas in pure alkali at these current densities passivation ensues within a short time. In the presence of SO_4^{2-} ions corrosion takes place uniformly over the whole electrode surface.

DISCUSSION

In strong alkaline solutions (5–10 *N*) at 90°, both in the absence and in the presence of Cl^-, SO_4^{2-}, and CO_3^{2-} ions, an iron electrode is passivated at a sufficiently high current density, and oxygen starts to be evolved from it with simultaneous dissolution of the iron to form the ferrate ion. The latter process takes place at a low rate, and ceases when a certain ferrate concentration is reached in the anode compartment. This points to some reversibility of the process or to the participation of the dissolved corrosion products in strengthening the passivating film.

Chloride ions influence the dissolution of iron in dilute solutions of alkali. Both in the presence and the absence of Cl^- ions, the velocity of this process is greater at 90° than at room temperature, apparently in conformity with the temperature coefficient of this electrochemical reaction.

The dissolution of iron in alkaline solutions can take place by two mechanisms[1,2] with the adsorption of hydroxyls (or oxygen atoms) as a preliminary stage (first mechanism), and more slowly without the participation of hydroxyls (second mechanism). The reaction is inhibited by the adsorption of oxygen which we term passivating, and which is distinguished from the above-mentioned adsorption of OH probably by a more thorough dehydration of the adsorbed layer and by the higher valency of the iron combined with the oxygen. In this connection it could be expected that the displacement of OH from the metal surface by anions, when the concentration of the latter is increased or that of the OH^- ions is decreased, would lead to activation of the metal only under conditions such that the passivating effect of the oxygen predominates during adsorption of OH, for example at high potentials. When, however, the activating effect of the OH predominates, *e.g.* at low potentials and high OH^- concentrations, the dissolution of iron should be retarded by the displacement of adsorbed OH by anions.

In fact, dissolution of iron takes place by the first mechanism at low current densities and not very low alkali concentrations, and either the overpotential of this process increases or the passivating current density decreases on addition of relatively large quantities of Cl^- and SO_4^{2-} ions to the alkali solutions. At low current densities, for example, a tenfold increase in the Cl^- concentration in 0.05 *N* KOH raises the overpotential of the anodic dissolution of iron, occurring by the first mechanism, by 0.06 V; *i.e.* Cl^- passivates the iron (Fig. 3). On the other hand, at higher potentials, when dissolution takes place by the second mechanism, an increase in the Cl^- concentration greatly lowers the overpotential; *i.e.* Cl^- activates the iron. A tenfold increase in OH^- concentration at low concentrations raises the overpotential of the reaction taking place by the second mechanism by about 0.2 V. At high alkali concentrations an increase in the alkali concentration in the presence of SO_4^{2-} leads to an increase in the minimum current density for passivation; *i.e.* alkali activates the iron electrode. These facts are in good agreement with the view that adsorbed hydroxyls have a dual role in the corrosion of iron in alkali and that the effect of anions on this process is associated with their adsorption.

On this view it is clear that activation and passivation of iron are determined by the ionic concentration ratios Cl^-/OH^- and SO_4^{2-}/OH^- as well as by the electrode potential. The activating effect of Cl^- ions on iron at high potentials becomes appreciable at concentration ratios > 1. In the case of SO_4^{2-} ions the same activation of the surface of an iron electrode by the anions takes place at an OH^- concentration which is only 2% of that in the case of Cl^- ions.

Comparison of our curves at 90° with anodic curves obtained at room temperature[1] shows that raising the temperature to 90° produces an approximately hundredfold increase in the current density required for the anodic passivation of iron activated by chloride anions. Such an increase in the rate of dissolution observed at high temperatures can be explained by the fact that in our experiments no pitting was observed, and dissolution of iron took place over a larger part of the surface than in the earlier experiments[1]. If it is remembered that at room temperature anodic dissolution takes place only at 1% of the electrode surface, the passivation current densities are found to be the same at the two temperatures. It is very probable that the first stage in the dissolution of iron by the second mechanism consists in the electrochemical adsorption of anions (*e.g.* Cl^-, SO_4^{2-}).

SUMMARY

1. It is established that chloride and sulphate ions exert both an activating and a passivating action on an iron anode in alkaline solutions. The nature of the effect is determined by the electrode potential and the alkali concentration.
2. The results obtained are consistent with the view that the rate of the anodic process occurring on iron in alkaline solutions is affected by the adsorption of anions, and in particular that the adsorption of hydroxyls has a dual (passivating and activating) action on this process, depending on the potential and the range of alkali concentrations. The data are consistent with the view that iron dissolves in alkaline solutions by two mechanisms.
3. Rapid corrosion of iron anodes under the activating influence of chloride ions is observed at alkali concentrations not exceeding 0.5 *N*.

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EFFECT OF TITANIUM ADMIXTURES ON THE SURFACE TENSION OF NICKEL AND COBALT AND ON THEIR INTERFACIAL TENSION WITH ALUMINIUM OXIDE

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Nickel and cobalt are used as cementation metals in the preparation of hard and heat-resistant alloys based on refractory and hard compounds of titanium: carbide, nitride, and boride.

When these alloys are prepared by the powder method, by impregnation or sintering in the presence of a liquid phase, the cementation metal is in the liquid state and its surface properties are largely responsible for the quality of the product and therefore also for those of the finished article. The effect of titanium on the surface properties of liquid nickel and cobalt is thus of considerable interest.

A study is presented here of the effect of titanium admixtures on the surface tension of liquid cobalt and nickel and also on the interfacial tension at the boundary between these melts and solid aluminium oxide.

EXPERIMENTAL

Surface tension and contact angles were determined by the sessile-drop-method with an apparatus already described[1,2].

The alloys were prepared using nickel and cobalt of high purity (99.99%) and iodide titanium (total impurity less than 0.07%), in an arc furnace with a cooled copper hearth, under argon.

Even the very first experiments revealed that titanium has a considerable interfacial activity in the present systems. Our usual method of calculating the surface tension from the maximum diameter of the drop and its distance below the apex[3] could not be applied in this case because the maximum diameter depends quite appreciably on the wetted perimeter at contact angles close to 90°. We used Bashforth and Adams' tables[4] to calculate the surface tension. For practical reasons, it was found convenient to measure the distances x and z for an angle $\varphi = 60°$ (see Fig. 1).

The surface tension is calculated from the formula

$$\sigma = \frac{b^2}{\beta}\Delta\rho g,$$

where b is the radius of curvature at the apex of the drop;

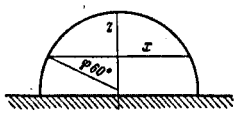

Fig. 1. Calculation of the surface tension from the profile of a drop.

β is a dimensionless parameter which describes the shape of the drop and depends uniquely upon x/z; $\Delta\rho$ is the difference in density between the phases in contact; g is the acceleration due to gravity.

The calculation of surface tension from Bashforth and Adams' tables is somewhat tedious because the tables do not give directly the variation of β with x/z for the required angle φ. The numerous interpolations needed to establish this dependence and to evaluate b make the method unattractive. In order to avoid this difficulty we constructed a new table (based on Bashforth and Adams' tables) of Φ as a function of x/z, as had previously been done in ref. 3 for $\varphi = 90°$. In Table 1 the function

$$\Phi = \frac{b^2}{\beta(2x)^2}$$

for $\varphi = 60°$ is expressed directly in terms of x/z.

In terms of this function we may evaluate the surface tension from the formula

$$\sigma = \Phi(2x)^2\Delta\rho g.$$

The precision of the method in the present case is 3–5%.

TABLE 1. Values of the function $\Phi = f(x/z)$ for $\varphi = 60°$ (sessile drop method).

x/z	0	1	2	3	4	5	6	7	8	9
1.89	0.2790	2770	2751	2733	2715	2696	2677	2661	2644	2627
1.90	0.2611	2594	2578	2563	2547	2532	2517	2502	2488	2473
1.91	0.2459	2445	2431	2418	2405	2392	2379	2366	2353	2341
1.92	0.2329	2317	2305	2293	2282	2270	2257	2244	2231	2218
1.93	0.2205	2193	2181	2169	2157	2145	2134	2122	2111	2100
1.94	0.2089	2078	2068	2057	2047	2037	2027	2018	2008	1998
1.95	0.1988	1979	1970	1961	1952	1943	1934	1926	1917	1907
1.96	0.1898	1888	1879	1870	1861	1852	1843	1835	1826	1818
1.97	0.1809	1801	1793	1785	1777	1770	1762	1754	1747	1740
1.98	0.1732	1725	1718	1711	1704	1697	1690	1684	1677	1670
1.99	0.1663	1656	1648	1641	1634	1628	1621	1615	1608	1602
2.00	0.1595	1589	1583	1577	1570	1564	1558	1553	1547	1541
2.01	0.1536	1530	1524	1519	1514	1508	1503	1497	1491	1485
2.02	0.1479	1473	1467	1462	1456	1451	1445	1440	1434	1429
2.03	0.1424	1419	1414	1409	1404	1399	1394	1389	1384	1380
2.04	0.1375	1370	1365	1360	1356	1351	1346	1341	1337	1332
2.05	0.1328	1323	1319	1314	1310	1306	1302	1297	1293	1289
2.06	0.1285	1281	1277	1273	1269	1265	1261	1257	1252	1248
2.07	0.1244	1240	1236	1232	1228	1224	1220	1216	1213	1209
2.08	0.1205	1202	1198	1194	1191	1187	1184	1180	1176	1172
2.09	0.1169	1165	1161	1158	1154	1150	1146	1143	1140	1136
2.10	0.1132	1129	1126	1122	1119	1116	1113	1110	1106	1103
2.11	0.1100	1097	1093	1090	1087	1084	1081	1078	1075	1072
2.12	0.1069	1066	1064	1061	1058	1055	1052	1050	1047	1044
2.13	0.1041	1037	1035	1032	1029	1026	1023	1020	1017	1015
2.14	0.1012	1009	1007	1004	1001	09985	09959	09931	09905	09879
2.15	0.09853	09826	09802	09777	09751	09727	09703	09677	09654	09631
2.16	0.09606	09584	09561	09534	09514	09489	09465	09441	09417	09393
2.17	0.09370	09346	09323	09301	09278	09256	09234	09212	09190	09168
2.18	0.09147	09122	09098	09073	09049	09026	09002	08979	08956	08933
2.19	0.08910	08888	08866	08844	08822	08802	08780	08759	08739	08718
2.20	0.08698	08679	08659	08639	08620	08601	08582	08564	08545	08526
2.21	0.08508	08490	08469	08448	08427	08406	08386	08366	08346	08326
2.22	0.08307	08287	08268	08249	08230	08211	08192	08173	08154	08136
2.23	0.08117	08099	08081	08063	08045	08028	08010	07993	07976	07960
2.24	0.07941	07924	07907	07890	07873	07857	07840	07824	07808	07792
2.25	0.07776	07760	07744	07729						