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UCRL-51681

A SIMPLE MODEL OF D_2 -DT- T_2 EQUILIBRIUM AT CRYOGENIC TEMPERATURES

P. C. Souers
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October 21, 1974

MASTER

Prepared for U.S. Atomic Energy Commission under contract No. W-7405-Eng-48

LAWRENCE LIVERMORE LABORATORY

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Printed in the United States of America

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**1-50
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**\$4.00
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A SIMPLE MODEL OF D_2 -DT- T_2 EQUILIBRIUM AT CRYOGENIC TEMPERATURES

Abstract

The literature on cryogenic properties of mixtures of hydrogen isotopes is reviewed. Liquid solutions of H_2 , HD, and D_2 appear totally miscible, but there is evidence of possible phase separation in the solid state. Using phase diagram data for H_2 , DH, and D_2 , estimates are made of the behavior of D_2 -DT, DT- T_2 , and D_2 - T_2 mixtures at cryogenic temperatures. A complete phase diagram

is assembled for the three-component DT system. Based on this diagrammatic model, a D/T ratio of 1.63 is required in the gas to yield a ratio of 1.00 upon liquefaction. Absence of reaction rate data makes it impossible to estimate the chemical stability of the isotopic species DT. Low-temperature gas chromatography is recommended as the best means of isotopic separation, should this be necessary.

Introduction

The energy crisis in this country has spurred great interest in developing laser-initiated hydrogen fusion as a new power source. The target substance for the high-energy experiments aimed at meeting this energy goal is expected to be DT because it provides the most easily initiated nuclear reaction. The cryogenic form is desirable to enable the DT to be shaped into various target geometries.

Two factors complicate DT target work compared to that done with D_2 alone. First, T is radioactive, decaying into He^3 , a beta particle, and an anti-neutrino. The beta particle, with a mean energy of 5.65 keV, is capable of causing

radiation damage or catalyzing reactions. Second, DT normally is delivered not as a single compound but as a three-component mixture of D_2 , DT, and T_2 , probably equilibrated by beta radiation.

In this report, we examine the cryogenic behavior of this three-component system. The three compounds, of course, possess slightly different physical properties. For example, the triple points for D_2 , DT, and T_2 occur at 18.72, 19.71, and 20.62 K, respectively, marking the beginning of the temperature range of cryogenic interest. A list of other pertinent physical properties, many estimated for DT and T_2 from the nonradioactive isotopes, is given in the Appendix.

DT Characteristics

CHEMICAL EQUILIBRIUM CONSTANTS

The DT chemical equilibrium constant, Q , has been calculated from thermodynamic considerations for the reaction¹

The mole percent DT is

$$(DT) = \frac{100 \sqrt{Q}}{2 + \sqrt{Q}}. \quad (2)$$

Calculated equilibrium constants and mole percentages for 50-50 D-T mixes are given in Table 1. Two important points should be noted. First, the DT equilibrium constant below 25 K has not been calculated. Extrapolation to a value of 1.8 at the triple point (19.75 K) seems reasonable, but DT behavior at 4.2 K is not at all obvious. Second, other isotopic combinations of hydrogen are quite different. For example, there is 36.6 mol% HD in an H_2 -HD- D_2 mixture and 19.7 mol% HT in H_2 -HT- T_2 for 50-50 atomic mixes at 50 K. There appear to be dangers in simulating DT with other isotopic combinations.

Table 1. Calculated equilibria for the reaction $D_2 + T_2 \rightleftharpoons 2 DT$.

Temperature, K	Chemical equilibrium constant (Q)	Concentration for 50-50 D-T mix, mol%		
		DT	D_2	T_2
1000	4.00	50.0	25.0	25.0
300	3.82	49.4	25.3	25.3
200	3.69	49.0	25.5	25.5
100	3.32	47.4	26.2	26.2
50	2.60	44.6	27.7	27.7
25	1.95	41.1	29.5	29.5
19.7	1.80 ^a	40.2 ^a	29.9 ^a	29.9 ^a

^a Estimate.

Few experimental data have been collected on equilibrium constants. Three D-T measurements, from 77 to 299 K, agree with the calculated equilibrium constants.² However, H-T experiments give various values, depending on the pressures and impurities involved.^{2,3}

CHEMICAL EQUILIBRIUM RATES

No D-T equilibrium rate data for Eq. (1) have been measured at any temperature. Tritium researchers at LLL report that the equilibration time is "fast" — probably on the order of minutes.⁴ It is felt that the β -particle causes this fast equilibration. Moreover, the reaction is quite complex, as demonstrated in a radiation-induced H-D rate study where Kr and Xe were found to have strong influence on the exchange rate.⁵

The chemical equilibrium rate is important because it indicates whether a pure isotopic form can or cannot be permanently isolated. If not, and three components are present, slow freezing will produce a nonuniform isotopic composition of the solid.

CRYSTAL STRUCTURE

Early Soviet x-ray work claimed that solid H_2 , D_2 , and T_2 at 4.2 K possessed tetragonal lattices.⁶ However, later studies showed a hexagonal-close-packed (hcp) structure for solid H_2 ,⁷⁻⁹ HD,¹⁰ D_2 ,⁹ and T_2 .¹¹

As the temperature is lowered from 4.2 K, the crystal structure changes from

hcp to a face-centered-cubic (fcc) configuration. This structural change has been noted for H_2 ,⁷⁻⁹ HD,¹⁰ and D_2 .¹¹ A small volume change (1.3%) has been measured for this phase transition in H_2 ,¹² and the transition temperature shows considerable hysteresis.^{8,9}

The hcp-to-fcc transformation, sometimes called the λ -anomaly, is an extreme function of the concentration of molecules with a rotational quantum number of $J = 1$; i.e., ortho- H_2 and para- D_2 (o- H_2 and p- D_2). The more of this component, the higher the transition temperature. An extrapolation of cooling data shows maximum transition temperatures of 2.8 K for o- H_2 and 3.8 K for p- D_2 .⁹ Neither form occurs pure in nature. Room temperature H_2 and D_2 (called normal, n) quenched without change of o-p composition undergo the λ -anomaly at 1.6 K and <1 K, respectively. Transformation to low-temperature equilibrium (abbreviated e) forms would lower the λ -anomaly temperature.

One might postulate that n- T_2 would undergo the transformation at 3 to 3.5 K, with cryogenic e-forms transforming at lower temperatures. Although no data are available for mixed hydrides, it appears that the λ -anomaly will not be a factor in targets fabricated at 4.2 K and higher.

PHASE SEPARATION IN LIQUID STATE

Studies of the H_2 - D_2 system between 30 and 80 mol% D_2 indicate that the liquids are miscible.¹³⁻¹⁵ The partial properties are to first-order additive (i.e., regular). A reduction in e- H_2 /e- D_2 volume of about -0.8% resulted

when the liquids were mixed.¹³ A similar volume reduction (about -0.5%) was found for n- H_2 /n- D_2 .¹⁴ and the excess heat of mixing and entropy were measured.¹⁵ Slight volume deviations also occurred upon mixing equal parts of liquid D_2 and T_2 .¹⁶ A positive volume increase (0.2 to 0.7%) was found in the mixture experiment, but results were complicated by the simultaneous chemical reaction of Eq. (1).

The absence of unusual behavior in the liquid phase is reflected by the absence of azeotropic points on the e- H_2 /e- D_2 liquid-vapor curve from 14 to 75 mol% D_2 .¹⁷ There is every reason to believe, therefore, that the D_2 -DT- T_2 system will form a single solution.

PHASE SEPARATION IN SOLID STATE

The issue of phase separation may be more complex for solid hydrogen. Indeed, the phase rule predicts as many as five phases for a three-component system. Three, then, might be solid phases.

Soviet x-ray studies claimed evidence of two solid phases for H_2 - D_2 ,¹⁸ H_2 -HD, and HD- D_2 ¹⁹ at 4.2 K. However, American work soon disputed this claim. Steady-state nuclear magnetic resonance showed a single Gaussian line for 0 to 85% n- D_2 in n- H_2 solutions over the temperature range 3 to 16.4 K.²⁰ Below 3 K, composite lines were observed, but no conclusions were drawn as to phase separation or hcp-to-fcc transformation. Further evidence was obtained from heat-capacity and temperature-time measurements at a constant heating rate.²¹ The form p- H_2 was used to avoid heating

effects due to the *o-p* transformation. Miscible solid solutions were found from 8 K to the melting point for 20 to 85% $n\text{-D}_2$ in $p\text{-H}_2$. No eutectic points were discovered in the liquid-solid curve.

Recent Soviet thermal studies have confirmed American claims of solid-phase miscibility. These studies of the phase diagrams of $\text{H}_2\text{-D}_2$,^{17,22} $\text{H}_2\text{-HD}$,²² and HD-D_2 ²² have resulted in cigar-shaped liquid-solid curves with no evidence of eutectic points. Theoretical studies of $\text{H}_2\text{-D}_2$ miscibility predict phase separation below 4 K only.²³⁻²⁵

However, the American scientists who first discovered solid-phase miscibility above 4.2 K have cast some doubt upon the issue.²¹ They believe the Soviets did see solid-phase separation as a result of particular (but unknown) experimental conditions. This qualification keeps alive the possibility of phase separation due to beta particle action in $\text{D}_2\text{-DT-T}_2$ mixtures.

MODEL OF D-T ENRICHMENT DUE TO LIQUEFACTION AND FREEZING

Although the triple-point D-T phase diagram has not been experimentally verified, D-T enrichment effects can be estimated from known H-D behavior. Chemical reaction of the $\text{H}_2\text{-D}_2$ system is slow enough that the two phases can be studied adequately.

Vaporization¹⁷ and melting^{21,22} may be combined to yield a composite $\text{H}_2\text{-D}_2$ phase diagram (Fig. 1). The temperature-mole% diagram lies along the triple line. It is not isobaric, but runs from H_2 vapor at one end to D_2 vapor at the other. Maximum vapor pressure for about 80% D occurs at 17.9 K and 18.9 Kpa (142

Torr).¹⁷ This pressure is 5% higher than the expected theoretical value obtained by adding partial pressure, 18.0 Kpa (135 Torr). Since the curves all close at the composition endpoints, there is no ambiguity in obtaining mixture data from horizontal phase lines. As shown in Fig. 1, a 50-50 gas mixture at 17.9 K will yield an 80% deuterated liquid and an 87% deuterated solid.

Melting data for the $\text{H}_2\text{-HD}$ and HD-D_2 systems²² illustrate an important empirical point, which allows estimates to be made of phase-diagram "cigar" shapes. The vertical height at 50-50 mix of the solid-liquid line "cigar" is not linear with the difference in triple points between any two components studied. For $\text{H}_2\text{-D}_2$, $\text{H}_2\text{-HD}$, and HD-D_2 , "cigar" thicknesses at the 50-50 line are 0.60, 0.15, and 0.10 K and differences in triple points are 4.9, 2.8, and 2.1 K, respectively. Employing this algorithm, we expect the D-T solid-liquid "cigars" to be quite thin. For $\text{D}_2\text{-T}_2$, $\text{D}_2\text{-DT}$, and DT-T_2 , estimated "cigar" thicknesses at the 50-50 line are 0.09, 0.04, and 0.03 K, respectively. As a further empirical

Fig. 1. Triple-line phase diagram for $n\text{-H}_2$ and $n\text{-D}_2$.

point, Fig. 1 shows about 1/3 of the solid-liquid "cigars" to be above the line joining the two triple points.

Recalling that vapor pressures are almost ideal,¹⁷ the gas lines for the various D-T combinations can be calculated assuming ideal behavior. (A liquid mix is converted to ideal partial pressures, which are reconverted back to gas compositions.) Liquid-gas "cigar" thicknesses at the 50-50 line for D_2 - T_2 , D_2 -DT, and DT- T_2 are estimated to be 0.30, 0.08, and 0.07 K, respectively. These "cigars" all lie above the line joining each pair of triple points. For all of these estimates, we ignore o-p composition because H has very little effect on vapor pressures at a given temperature.

Finally, the three sets of estimated two-component phase diagrams are combined to form the triangular phase diagram prism shown in Fig. 2. The "cigars" are somewhat exaggerated for clarity. We now have solid, liquid, and gas surfaces; the first bowing downward and the latter two bending upward. At each corner of the prism, all lines converge to the appropriate triple point. Each side of the prism is a two-component phase diagram.

Since 50-50 D-T mixes are of interest as laser target fuel, let us simplify the prism by considering the liquid to be fixed at 50-50 D-T. This is indicated by a line from the DT triple point (19.71 K) to the 50-50 liquid point on the D_2 - T_2 phase plane at 19.67 K. The line bows upward in the center by an amount our elementary model cannot calculate. For simplicity, however, we may consider the triple lines of interest to occupy an isothermal cut at about 19.75 K.

Fig. 2. Calculated triple-line phase diagram for D_2 -DT- T_2 .

The solid and gas lines originate at the DT triple point and run (at 19.75 K) to some points on the D_2 - T_2 phase plane. The 19.75-K tie line on the D_2 - T_2 phase diagram yields a solid point of 35 mol% D_2 -65% T_2 and a gas point of 65% D_2 -35% T_2 . As shown in Fig. 2, the end points can be connected to yield approximate solid and gas lines; again, with unknown curvatures. Also, the "cigars" formed are not closed at one end, a common feature of three-component phase diagrams.

A second reference line is required across the 19.75-K triple surface to mark chemical equilibrium of the three components, as defined in Eq. (1). Figure 3 shows two such lines, one for room temperature ($Q = 3.82$) and one for 19.75 K ($Q \sim 1.8$ by extrapolation of experimental data). Use of the room temperature line

Fig. 3. Calculated cross section of D_2 -DT- T_2 prism at 19.75 K.

implies no adjustment in equilibrium upon cooling, probably unlikely in view of the expected catalytic effect of the beta particle. The 19.75-K line assumes equilibration to that temperature.

Intersection of the phase lines with the appropriate equilibrium line yields the desired relations, summarized in Table 2. There is considerable T enrichment as the mixture cools from gas to liquid to solid. The apparent symmetry of the results must be considered coincidental at this time.

Whatever mode of target fabrication is used, it is probably safe to predict that a slow cooling of gas to liquid will be employed, and this will require correction for isotopic enrichment. However, the laser target probably will initiate as a small liquid drop,²⁶ and, if it freezes quickly, the total amount of D and T will be conserved, thereby eliminating the necessity of correcting for liquid-to-solid enrichment. But, if the droplet freezes slowly by heat conduction to the atmosphere

around it, internal isotopic enrichment will occur. The exterior, first to freeze, will be T rich, and the interior, last to freeze, will be D rich.

ISOTOPIC SEPARATION

Of course, one way to avoid the potential problems of a three-component system is to obtain the single component, DT. The important unknown, however, is the rate at which this compound will equilibrate to D_2 and T_2 and possibly offset efforts at isotopic separation.

The most obvious synthetic method for producing DT is the classic procedure for preparing HD, which is produced in 85% yield by the chemical reaction^{27,28}

This reaction is followed by cryogenic distillation to yield HD of 99.8% purity.²⁸⁻³⁰ For DT, the procedure would have to be amended to a tritide salt and deuterated water. Even so, exchange reaction would produce some amount of T_2O -tritium in its most hazardous form. This means the cryogenic distillation of D_2 -DT- T_2 , covering only 2 K at the triple

Table 2. Fractionation results at 19.75 K for three-component system and a liquid D/T ratio of 1.00.

Chemical equilibrium constant (Q) (equiv. temp., K)	Physical state	Concentration, mol%			D/T ratio
		D_2	T_2	DT	
Q = 1.6 (19.75)	Gas	43	10	48	1.63
	Liquid	30	30	40	1.00
	Solid	20	12	33	0.64
Q = 3.82 ^d (300)	Gas	46	16	48	1.50
	Liquid	25.25	25.25	49.50	1.00
	Solid	16	30	48	0.65

^dAssumes no chemical re-equilibration upon cooling from room temperature to 19.75 K during the experiment.

points, would require great care as to temperature and safety control.

There are many other methods for the isotopic separation of hydrogen, but most are designed simply to yield a net enrichment of T, without regard to the molecular species. These methods include electrolysis in water, gas thermal diffusion, distillation of water, and chemical reaction or adsorption with another material.³¹

Adsorption (particularly low-temperature gas chromatography) appears to be the most sensitive and safe technique for DT separation. In this method, a mixture of isotopic hydrogen molecules (at 77 K) is passed with a carrier gas through a 2- to 7-m column of adsorbing material, usually alumina with or without a ferric oxide coat. Since heavier molecular species are more tightly adsorbed, a recorder on the outflow will show a series

of peaks with time, proceeding from the lightest to the heaviest species. The separation ability is usually described by a set of ratios, α , relating peak appearance times between two given species.^{32,33} A summary of eight sources yields ratios of 1.16 for DT/D_2 and 1.13 for T_2/DT .³⁴ This chromatographic technique is so sensitive, it is even possible to separate ortho- and para-forms of the same isotope.^{34,35}

Sample volumes in gas chromatography are typically quite small, although a special system capable of carrying a 0.02 m^3 [STP] load of hydrogen in 40 to 80 min has been described.³⁶ Moreover, greater efficiency may be possible at lower temperatures. A column of paramagnetic-free γ -alumina at 55 K is claimed to have recorded ratios of 3.6 and 2.4 for DT/D_2 and T_2/DT , respectively.³⁵

Conclusions

A model of the D_2 -DT- T_2 phase diagram has been constructed to consider the special problems of fabricating cryogenic laser targets. Under the best, and most likely, conditions, one will at least have to contend with T enrichment as the gaseous mixture is liquefied and frozen. To obtain a final 50-50 D-T target mix, knowledge of the D_2 -DT- T_2 phase diagram is required to establish initial gas composition. Under the worst condition, the solid mixture may split into separate phases, catalyzed by the beta particle. This could result in local D-T compositions far from the desired 50-50 mix, causing low neutron yield when the target is hit with the laser. Cracking and

lack of transparency may also result from such phase separation.

An obvious solution to three-component difficulties is to isolate only the molecular species, DT. At present, gas chromatography appears to be the best method of such isotope separation. However, the rate of chemical equilibration of DT to the three-component mixture has never been measured; although it is suspected to be fast because of beta particle catalysis. Unlike the phase diagram, the chemical equilibrium rate cannot be estimated. Such a measurement ranks high on the list of needed heavy-hydrogen research.

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Appendix

Cryogenic Properties of Hydrogen Isotopes

Table A-1 presents information on physical cryogenic properties of heavy hydrogen pertinent to this study.

Recommended National Bureau of Standards^{A-1} vapor pressures were used in calculating the vapor pressure values presented in Table A-2. Graphic interpolations to integral temperature values are used, resulting in fewer significant digits for these numbers. Also, DT vapor pressures are estimated from graphs of this property as a function of the mole weight. Vapor pressure decrease with increasing mole weight (at a given

temperature) is not linear, but slows with increasing mass. Hence, we expect DT vapor pressure to be closer to that of n-T₂ than expected from an averaging of D₂-T₂ values. Consequently, our estimated vapor pressures are 3 to 7% lower than those estimated by Thodos.^{A-2} There is no experimental data for DT, even for the triple point. Thodos calculated the vapor pressure of s-H₂ to be about 3% greater than that of n-H₂ and about 1% greater for D₂. Therefore, there is little orthopara effect.

Table A-1. Cryogenic properties of heavy hydrogen.

Physical property	H ₂	D ₂	DT	T ₂	Ref.
Molecular weight, Kg/mole × 10 ³	2.016	4.029	5.032	6.034	
Definition of normal (n) state (found at 298 K)	74.92% ortho (J ^a odd)	66.67% ortho (J even)	No thermodynamic difference between J-states	74.91% ortho (J-odd)	A-3
Triple-point temperature for n-form, K	13.957	18.71	19.71 ^b	20.62	A-4, -5
Triple-point pressure for n-form, kPa (Torr)	7.205 (54.04)	17.13 (128.5)	19.42 ^b (145.7) ^b	21.60 (162.0)	A-4, -5
Definition of equilibrium state (e) at triple point	0.0% ortho (J odd)	98.5 ortho (J even)	No thermodynamic difference between J-states	35% ortho (J odd)	A-3
Triple-point temperature for e-form, K	13.803	18.691	19.71 ^b	20.61 ^b	A-4, -5
Triple-point pressure for e-form, kPa (Torr)	7.042 (52.82)	17.13 (128.5)	19.42 ^b (145.7) ^b	21.60 ^b (162.0) ^b	A-4, -5
Critical temperature of n-form, K	33.19	38.34	39.42 ^b	40.44 ^b	A-4

Table A-1 (continued)

Physical property	H ₂	D ₂	DT	T ₂	Ref.
Critical pressure of n-form, kPa (atm)	1315 (12.98)	1664.9 (16.432)	1770 ^b (17.5) ^b	1850.2 ^b (18.261) ^b	A-4
Density of n-compound at triple point, kg/m ³					
Solid	86.71	196.70	258 ^b	324 ^b	A-6
Liquid	77.21	173.95	224 ^b	273.9	
Gas	0.13	0.45	0.61 ^b	0.78	
Heat of fusion for n-compound at triple point, J/mol	117.1	196.6	235-260 ^b	260-280 ^b	A-6
Heat of vaporization for n-compound at triple point, J/mol	911.3	1287.6	1390-1420 ^b	1480-1530 ^b	A-6
n-form to triple-point e-form energy release, J/mol	1062	228	0	191	A-7
D ₂ -DT-T ₂ mixture: room temperature equilibrium for 50-50 D-T mix, %	—	25.3	49.4	25.3	A-8
D ₂ -DT-T ₂ mixture: triple-line equilibrium (19.75 K) for 50-50 D-T mix, %	—	29.9 ^b	40.2 ^b	29.9 ^b	A-8
D ₂ -DT-T ₂ mixture: n-form to triple-line (19.75 K) e-form energy release for 50-50 D-T mix, J/mol	—		19.3 ^b		A-7, -8

^aJ is the molecular rotational quantum number. It is important in this text only because there is a thermodynamic difference (with heat evolved) between rotational states of hydrogen molecules with identical nuclei. Apparently, there is no thermodynamic difference between rotational states of HD and by extrapolation here, DT. However, the J=1 form of HD rises from 0% at 20 K to an ever increasing fraction at higher temperatures. The form of HD, therefore, does change with temperature. For an example, see M. Trefler, A. M. Cappel, and H. P. Gush, Can. J. Phys. **47**, 2115 (1969).

^bEstimate.

Table A-2. Solid/liquid-gas vapor pressures of hydrogen isotopes.

Temperature, K	Vapor pressure, kPa (Torr)				
	H ₂	HD	D ₂	DT ^a	T ₂
4.2	4.7×10^{-8} (3.5×10^{-7})				
4.5	2.4×10^{-7} (1.8×10^{-6})				
5	2.5×10^{-6} (1.9×10^{-5})				
6	1.6×10^{-4} (1.2×10^{-3})				
7	2.0×10^{-3} (0.015)				
8	0.013 (0.10)				
9	0.065 (0.49)				
10	0.24 (1.8)	0.037 (0.28)	6.7×10^{-3} (0.05)		
11	0.68 (5.1)	0.13 (0.99)	0.028 (0.21)		
12	1.67 (12.5)	0.39 (2.94)	0.097 (0.73)		
13	3.87 (29)	0.995 (7.46)	0.285 (2.14)		
13,957	7.205 (54.04)	2.17 (16.3)	0.69 (5.2)		
14	7.39 (55.4)	2.24 (16.8)	0.725 (5.44)	0.33 (2.5)	0.20 (1.5)
15	12.7 (95)	4.59 (34.4)	1.64 (12.3)	0.80 (6)	0.57 (4.3)
16	20.44 (153.3)	8.69 (65.2)	3.39 (25.4)	1.8 (13.5)	1.3 (9.4)
16,60	26.7 (200)	12.4 (92.8)	5.1 (38)	2.8 (21)	1.93 (14.5)
17	31.36 (235.2)	14.99 (112.4)	6.48 (48.6)	3.6 (27)	2.6 (19.5)
18	46.12 (345.9)	23.49 (176.2)	11.6 (87.2)	6.7 (50)	5.1 (38)
18,72	60.0 (450)	32.0 (240)	17.13 (128.5)	10.4 (78)	8.0 (60)
19	65.43 (490.8)	35.22 (264.2)	19.44 (145.8)	12.1 (91)	9.3 (70)
19,71	82.7 (620)	46.0 (345)	26.4 (198)	19.42 (145.7)	13.4 (104)
20	90.08 (675.7)	50.93 (382)	29.44 (220.8)	20.50 (154)	16.0 (120)
20,62	109 (815)	62.7 (470)	37.3 (280)	26.50 (199)	21.60 (162)
21	121 (910)	71.31 (534.9)	42.97 (322.3)	31 (233)	25.3 (190)
22	157 (1180)	97.12 (728.5)	60.71 (455.4)	45 (338)	37.3 (280)
23	204 (1530)	129.2 (969)	83.44 (625.9)	64 (480)	53.3 (400)
24	257 (1930)	168.2 (1262)	111.9 (839.5)	88.50 (664)	74.7 (560)
25	320 (2400)	215.2 (1614)	146.9 (1102)	117.50 (881)	100 (750)

^aEstimated.

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