MAXIMUM DENSITY OF MILK

by

THOMAS MILTON MEDVED

B. S., Kansas State College
of Agriculture and Applied Science, 1952

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1956

TABLE OF CONTENTS

INTRODUCTION

To understand a system as a whole, it is necessary to have a knowledge of the basic fundamental properties of the system. In order to understand the system of milk, a knowledge of its physical properties such as density, viscosity, surface tension, index of refraction to name a few must be understood. It is the purpose of this investigation to determine precisely the density of milk between the temperatures of 8.000° and -6.750°C. The upper limit of 8.000°C. was chosen to be well above the maximum density of water at 4.00°C. Minus 6.750°C. was as low as milk could be supercooled without freezing. The density above 8.000°C. has been studied extensively and follows a smooth curve being almost linear. (Rutz et al. 9).

The effect of water having a maximum density at 4.00°C. on milk at the same temperature was not quite clearly understood. Rutz et al. (9) reported indications of irregular changes in the density of milk at temperatures near 4.00°C. This has been investigated further in this study.

Other authors have reported the maximum densities of milk as being at different temperatures. Davies (2) reported the maximum density of milk is -0.3°C. Olson (7) reported the maximum density of milk is -0.56°C. No references for these values were quoted by them.

By supercooling milk below its freezing point the maximum density of whole homogenized pasteurized milk was investigated. The maximum density of skim pasteurized milk was also determined.

The effect of diluting whole homogenized milk with various percentages of water shifted the maximum density toward the maximum density of water. This shift was proportional to the amount of dilution, coming closer to the maximum density of water with greater percentage of water added.

Most of the experiments on the density of milk in relation to temperature were done with a lactometer and the information is used primarily for calculation of total solids in milk. (5), (10), (1), (6).

EXPERIMENTAL

Method of Density Measurement

Densities were measured using the hydrostatic weighing method, as described in Weissberger (12). Glass sinkers were made of pyrex glass tubing approximately 28 ml. in diameter. They were made to displace over 100 ml. of fluid. Lead weights were placed inside to overcome the effect of buoyancy. The total weight of each bulb was around 150 gms.

A bulb was suspended from an analytical balance from which one pan was removed and a nichrome wire link suspended in its place. This link passed through a hole in the bottom of the balance, and connected to a fine nichrome wire which was attached to the bulb. The bulb was immersed in the liquid contained in a test tube approximately 35 mm. by 250 mm., which was suspended in a constant temperature bath. The relative closeness of the bulb to the inside of the test tube provided very good stirring action when the balance was deliberately offset by adding or subtracting weight.

Densities were calculated by the relationship

$$d = \frac{(W_v - W_m)}{V_i};$$

W_v = Weight in vacuum; W_m = Weight in milk; V_i = Volume of bulb.

$W_v - W_m$ = Weight of displaced liquid.

Calibration of Thermonitor and Thermometers.

A 5 ohm platinum resistance thermometer was used as primary source of temperature control. This was calibrated as described by Weber (11). A delta value of 1.502 was obtained.

The platinum resistance thermometer was used to calibrate Beckman differential thermometers and a Sargent Model S Thermonitor, which were used to control the bath temperature directly. The bath could be maintained at ±.001°C. at low temperatures, and ±.003°C. at higher temperatures. This was determined by observing the change in resistance of the platinum thermometer over a period of time.

Calibration of Density Bulb

The bulb was weighed in air of known density and calculated by successive approximations to weight in vacuum. This weight was usually around 150 gms. The bulb was then weighed in water at various temperatures and the volume of the bulb was found by the relationship

$$V_t = \frac{W_v - W_w}{D_w};$$

V_t = Volume of bulb at temperature T; W_v = Weight of bulb in vacuum; W_w = Weight of bulb in water at temperature T; D_w = Density of water at temperature T. The densities of water were taken from Dorsey (3). A coefficient of expansion for the bulb was obtained from the volume at various temperatures and the volume was calculated at any other temperature. This expansion was nearly linear.

The time required for the bulb to come to equilibrium temperature with the sample was determined. This was found to be not more than 15 minutes after the bath had reached the temperature desired.

Description of Apparatus

The bath was made from a porcelain pan, approximately 12 inches in depth and 15 inches in diameter. It was insulated with an inch of spun glass insulating material and encased in a wooden box. It was suspended beneath the balance on two pulleys and was counterbalanced by window weights which facilitated ease of raising and lowering bath when adjustments in alignment were necessary. The bath was insulated on top by a block of plastic foam, leaving only a hole for the nichrome link to pass through.

The bath was cooled with an SO_2 refrigeration system, which could be regulated by a system of cone pulleys to give varying degrees of cooling depending on the temperature at which measurements were to be made, and the temperature of the room.

The balance was supported on a three inch channel beam which was mounted on a concrete pillar.

The clamp that held the sample tube in place was also suspended from the three inch channel beam.

The Sargent Model S Thermonitor was modified in that the 5000 ohm potentiometer was replaced by three decade dials of 1000 ohm, 100 ohm and 10 ohm steps, respectively. This insured a more reproducible setting by circumventing error in setting the one 5000 ohm potentiometer. An ammeter was also installed in series with the controlling heater. This enabled more accurate settings in calibration in that a definite reading could be made as to the power supplied to the heater, instead of judging by the brightness of the heater light.

Description of Milk

The mixed milk used in these experiments was from the Kansas State College herd. It was processed by the Dairy Department using a 300 gallon per hour Cherry Burrell viscolizer. The milk was whole homogenized pasteurized, or non-homogenized pasteurized, and skim pasteurized. It was not used within ten hours after processing.

The milk was analyzed for fat by the Mojonnier method and milk used had a fat content of 3.60 $\pm$.15 per cent. The total solids was 12.68 $\pm$.25 per cent.

EXPLANATION OF PLATE I

Plate I shows the apparatus used in the measurements of density. The modified Sargent S Model Thermonitor is shown at the left.

PLATE I

EXPLANATION OF PLATE II

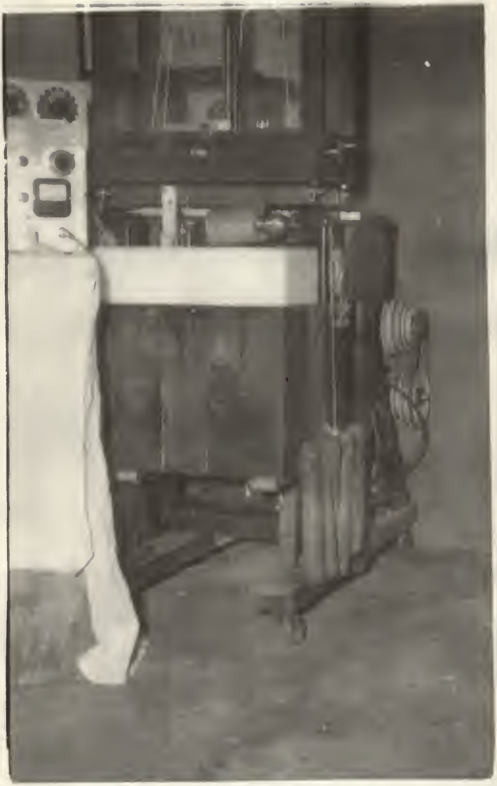
Plate II shows a close-up of the suspension of the glass sinker in a milk sample. The constant temperature bath is lowered, and the top insulation has been removed.

PLATE II

EXPLANATION OF PLATE III

Plate III shows the apparatus ready for use. The bath is raised in position, and the top insulation is in place.

PLATE III



RESULTS AND DISCUSSION

Plate IV shows the four least squares regression lines fitted to the data in Table 1. The coefficients of correlation were calculated and shown in Table 1. From these observations it was shown that to seven places there is no irregularity in the density of milk at temperatures near the maximum density of water.

Table 1. Density of milk between 3° and 5° C.

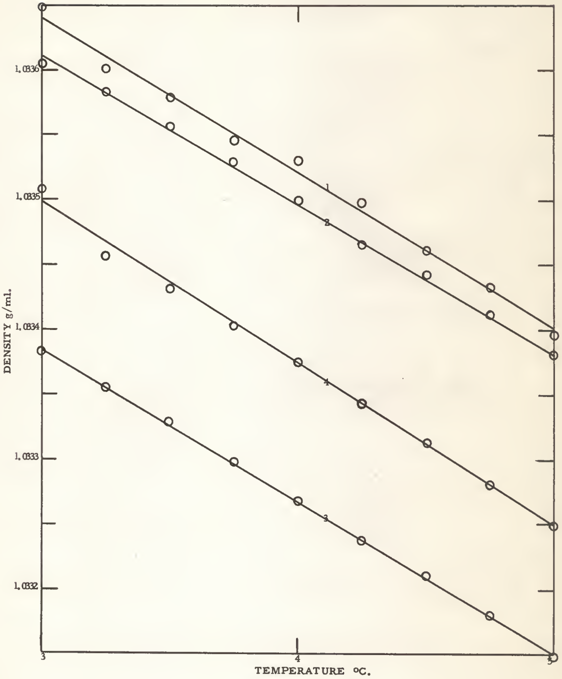
Temp.	Sample 1 processed 7-27-55 Density	Sample 2 processed 8-1-55 Density	Sample 3[b] processed 8-5-55 Density	Sample 4 processed 8-8-55 Density
3.00	1.033604	1.033383	1.03508	1.033649
3.25	1.033585	1.033355	1.033456	1.033601
3.50	1.033561	1.033328	1.033431	1.033578
3.75	1.033529	1.033298	1.033403	1.033545
4.00	1.033499	1.033268	1.033376	1.033530
4.25	1.033464	1.033238	1.033342	1.033498
4.50	1.033442	1.033210	1.033312	1.033461
4.75	1.033411	1.033179	1.033281	1.033433
5.00	1.033380	1.033149	1.033249	1.033396
r[a]	.998	.999	.998	.997

[a]Coefficient of correlation to least squares regression line.
[b]Non-homogenized sample.

EXPLANATION OF PLATE IV

Plate IV shows the data from Table 1. Densities of four different samples of milk between 3° and $5^{\circ}C$. The lines were fitted by method of least squares. No's. 1, 2 and 4 are whole homogenized pasteurized milk. No. 3 is whole non-homogenized pasteurized milk.

PLATE IV


1.0336
1.0335
1.0334
1.0333
1.0332
DENSITY g/ml.
1
2
4
3
3
4
5
TEMPERATURE °C.

The maximum density of milk was found by solving the least squares quadratic regression equation when the derivative was set equal to zero. For whole homogenized pasteurized milk, the maximum density for the milks of 11-28-55, 2-4-55, 12-28-55, were respectively, -4.90°, -5.15°, -5.17°C. These give an average of -5.07°C. These values are shown in Table 2 and plotted in Plate V.

When milk is diluted with water, the maximum density shifts toward the maximum density of water, and this shift is proportional to the concentration of the milk. This is shown in Plate VI.

Table 2. The density of various concentrations of milk

100% milk tested 11-28-55		100% milk tested 2-4-56		100% milk tested 12-28-55	
Temp.	Density	Temp.	Density	Temp.	Density
-3.25	1.035682	-4.50	1.035761	-4.00	1.035613
-3.50	1.035690	-4.75	1.035765	-4.25	1.035617
-3.75	1.035698	-5.00	1.035768	-4.50	1.035620
-4.00	1.035702	-5.25	1.035767	-4.75	1.035623
-4.25	1.035706	-5.50	1.035766	-5.00	1.035624
-4.50	1.035711			-5.25	1.035625
-4.75	1.035711			-5.50	1.035624
-5.00	1.035710			-5.75	1.035622
-5.25	1.035711			-6.00	1.035620
-5.50	1.035709				
-5.75	1.035697				
-6.00	1.035693				
-6.25	1.035692				
-6.50	1.035683				
-6.75	1.035682				
Calculated maximum density					
-4.90		-5.15		-5.17	
p[a] .986		.998		.966	

[a]Index of correlation of least squares quadratic regression equation.

Table 2. (cont.)

90% milk tested 11-26-55		80% milk tested 12-1-55		60% milk tested 12-1-55	
Temp.	Density	Temp.	Density	Temp.	Density
-2.50	1.031949	-1.50	1.028657	0.00	1.021331
-2.75	1.031953	-1.75	1.028667	-0.25	1.021337
-3.00	1.031957	-2.00	1.028670	-0.50	1.021341
-3.25	1.031961	-2.25	1.028675	-0.75	1.021343
-3.50	1.031972	-2.50	1.028681	-1.00	1.021346
-3.75	1.031974	-2.75	1.028684	-1.25	1.021351
-4.00	1.031968	-3.00	1.028686	-1.50	1.021347
-4.25	1.031977	-3.25	1.028686	-1.75	1.021349
-4.50	1.031966	-3.50	1.028685	-2.00	1.021352
-4.75	1.031969	-3.75	1.028685	-2.25	1.021352
-5.00	1.031967	-4.00	1.028677	-2.50	1.021351
-5.25	1.031963	-4.25	1.028677	-2.75	1.021342
-5.50	1.031958	-4.50	1.028674	-3.00	1.021338
-5.75	1.031956	-4.75	1.028670		
-6.00	1.031945	-5.00	1.028664		
Calculated maximum density					
	-4.05	-3.32		-1.73	
p^a	.987	.977		.959	

[a]Index of correlation of least squares quadratic regression equation.

Table 2. (cont.)

40% milk tested 12-2-55		20% milk tested 12-3-55		10% milk tested 7-30-55	
Temp.	Density	Temp.	Density	Temp.	Density
1.75	1.013891	3.25	1.006930	3.00	1.003384
1.50	1.013899	3.00	1.006944	3.25	1.003382
1.25	1.013907	2.75	1.006947	3.50	1.003385
1.00	1.013915	2.50	1.006948	3.75	1.003382
0.75	1.013918	2.25	1.006951	4.00	1.003379
0.50	1.013918	2.00	1.006954	4.25	1.003380
0.25	1.013921	1.75	1.006955	4.50	1.003374
0.00	1.013923	1.50	1.006957	4.75	1.003368
-0.25	1.013924	1.25	1.006955	5.00	1.003363
-0.50	1.013924	1.00	1.006949	5.25	1.003354
-0.75	1.013919	0.75	1.006942		
-1.00	1.013916	0.50	1.006941		
-1.25	1.013912	0.25	1.006936		
-1.50	1.013906	0.00	1.006930		
-1.75	1.013897				
-2.00	1.013891				
Calculated maximum density					
	-0.02		1.72		3.68
P^a	.999		.960		.988

[a]Index of correlation of least squares quadratic regression equation.

Table 2. (concl.)

100% skim milk tested 12-5-55		20% skim milk tested 12-6-55	
Temp.	Density	Temp.	Density
-1.00	1.037932	4.00	1.007484
-1.25	1.037939	3.75	1.007490
-1.50	1.037947	3.50	1.007491
-1.75	1.037949	3.25	1.007493
-2.00	1.037951	3.00	1.007496
-2.25	1.037953	2.75	1.007496
-2.50	1.037953	2.50	1.007494
-2.75	1.037951	2.25	1.007492
-3.00	1.037952	2.00	1.007492
-3.25	1.037951	0.75	1.007489
-3.50	1.037947	0.50	1.007485
-3.75	1.037945		
-4.00	1.037938		
Calculated maximum density			
	-2.60		2.25
p[a]	.974		.960

[a]Index of correlation of least squares quadratic regression equation.

EXPLANATION OF PLATE V

Plate V shows the densities of milk and diluted milk around the maximum density. The arrow represents the calculated point of maximum density. The data is fitted to second degree polynomial.

	concentration	date tested	temperature of maximum density	density at maximum density
A	100% milk	12-28-55	-5.17	1.035624
B	100% milk	2-4-56	-5.15	1.035768
C	100% milk	11-28-55	-4.90	1.035711
D	90% milk	11-26-55	-4.05	1.031970
E	80% milk	12-1-55	-3.32	1.028685
F	60% milk	12-1-55	-1.73	1.021349
G	40% milk	12-2-55	-0.02	1.013923
H	20% milk	12-3-55	1.72	1.006955
I	10% milk	7-30-55	3.68	1.003383
J	100% skim	12-5-55	-2.60	1.037952
K	20% skim	12-6-55	2.25	1.007492

Temperature increases to the right.

PLATE V

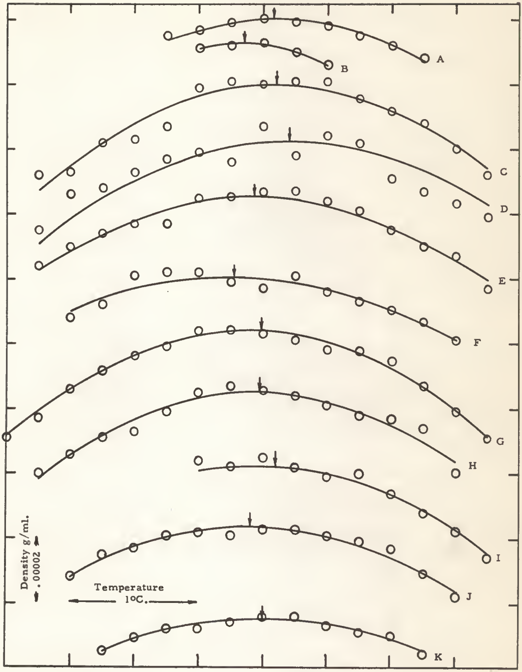


Table 3. Maximum density versus concentration[a]

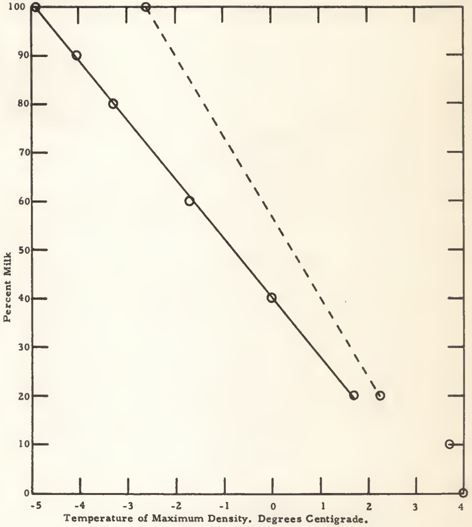
whole homogenized		:	skim	
% milk	Maximum density	:	% skim	maximum density
100[b]	-4.90		100	-2.60
90	-4.05		20	2.25
80[c]	-3.32			
60	-1.73			
40	-0.02			
20	1.72			
10[d]	3.68			

[a]This data was plotted in Plate VI. An eye fitted straight line was drawn between points.
[b]Using milk of 11-28-55. This milk was used for 90% dilution.
[c]Milk of 12-1-55. This milk used for 60, 40, and 20% dilutions.
[d]This is milk of 7-30-55, and of a different season than other samples, which may account for the non-proportionality as seen in Plate VI. No analysis of this sample was made.

EXPLANATION OF PLATE VI

Plate VI shows the percent milk plotted against temperature of maximum density. This is a linear proportionality and the lines are eye fitted curves. Dotted line indicates skim milk.

PLATE VI


100
90
80
70
60
50
40
30
20
10
0
Percent Milk
-5
-4
-3
-2
-1
0
1
2
3
4
Temperature of Maximum Density, Degrees Centigrade.

It is known that milk increases in density with age. The effect of this increase on the temperature of maximum density was not known. A study was made to determine this effect. Two samples of whole homogenized pasteurized milk were used. These samples were analyzed and found to have a fat content of 3.41 per cent and total solids of 12.29 per cent. Zero time was taken at the end of pasteurization. The densities at $-2.00^{\circ}C.$, and the temperature of maximum density are given in Tables 4 and 5, and shown in Plate VII.

The density increased very rapidly during the first nine hours, it then changed more slowly and continued to rise as long as measurements were made.

The temperature of maximum density also in general increased with age, with rate relations very similar to rates for increases in density.

Irregularities at 100 hours found for both density and temperature of maximum density were up to 300 times the error of density measurements. These irregularities may be due to the different seasons in which the milk was produced or to differences in the processing of the milk. An adequate study of these differences is beyond the scope of the present study. The existence of such irregularities makes useless any attempt at exact corrections for age.

Table 4. Densities for age versus maximum density

Sample 1. Processed 2-4-56

Age Temp.	10 hrs. Density	34 hrs. Density	58 hrs. Density
-3.00		1.035824	1.035927
-3.25		1.035830	1.035931
-3.50		1.035838	1.035934
-3.75		1.035840	1.035939
-4.00		1.035846	1.035943
-4.25		1.035849	1.035940
-4.50	1.035761	1.035852	1.035947
-4.75	1.035765	1.035852	1.035948
-5.00	1.035768	1.035844	1.035946
-5.25	1.035767	1.035846	1.035942
-5.50	1.035766	1.035836	1.035939
-5.75			1.035935
-6.00			1.035929
Calculated maximum density	-5.18	-4.51	-4.40

Table 4. (cont.)

Sample 1. Processed 2-4-56

Age	82 hrs.	130 hrs.	226 hrs.
Temp.	Density	Density	Density
-3.00	1.035922		1.036090
-3.25	1.035935	1.036009	1.036101
-3.50	1.035938	1.036014	1.036098
-3.75	1.035940	1.036017	1.036104
-4.00	1.035941	1.036021	1.036100
-4.25	1.035940	1.036025	1.036098
-4.50	1.035944	1.036027	1.036093
-4.75	1.035942	1.036028	1.036085
-5.00	1.035941	1.036027	
-5.25	1.035942	1.036023	
-5.50	1.035939	1.036019	
-5.75	1.035937	1.036016	
-6.00	1.035931		
Calculated maximum density			
	-4.37	-4.67	-3.77

Table 4. (cont.)

Sample 2. Processed 4-3-56

Age : Temp.	1 hr. Density	9 hrs. Density	24 hrs. Density	48 hrs. Density
-3.00		1.034560	1.034628	1.034688
-3.25		1.034570	1.034633	1.034695
-3.50		1.034578	1.034637	1.034697
-3.75		1.034582	1.034641	1.034699
-4.00		1.034585	1.034645	1.034698
-4.25		1.034587	1.034648	1.034690
-4.50	1.034483	1.034584	1.034645	
-4.75	1.034492	1.034583	1.034642	
-5.00	1.034497	1.034580	1.034637	
-5.25	1.034499	1.034576	1.034631	
-5.50	1.034501	1.034572	1.034624	
-5.75		1.034568		
-6.00		1.034564		
Calculated maximum density				
	-5.44	-4.48	-4.21	-3.67

Table 4. (concl.)

Sample 2. Processed 4-3-56

Age :	72 hrs. :	96 hrs. :	240 hrs.
Temp. :	Density :	Density :	Density
-2.00			1.034921
-2.25		1.034710	1.034926
-2.50		1.034716	1.034932
-2.75		1.034717	1.034935
-3.00	1.034714	1.034720	1.034937
-3.25	1.034716	1.034722	1.034939
-3.50	1.034716	1.034724	1.034939
-3.75	1.034718	1.034724	1.034938
-4.00	1.034715	1.034725	1.034938
-4.25	1.034714	1.034723	1.034937
-4.50	1.034713	1.034721	1.034932
-4.75		1.034718	1.034926
-5.00		1.034715	1.034922
-5.25		1.034710	
Calculated maximum density			
	-3.65	-3.74	-3.48

Table 5. Density versus age at -2.00 degrees centigrade

Sample 1		:	Sample 2	
Age in hrs.	Density	:	Age in hrs.	Density
10	1.035662		1	1.034260
34	1.035798		9	1.034528
58	1.035887		24	1.034608
82	1.035898		48	1.034669
130	1.035958		72	1.034694
226	1.036069		96	1.034704
			240	1.034921

EXPLANATION OF PLATE VII

Plate VII shows the combination of two graphs. The solid lines are a study of Temperature of Maximum Density versus the Age of the milk at various times. The dotted lines are a study of the Density versus Age, for two samples of milk at -2.00°C.

PLATE VII


1.036
1.035
Density g/ml
-5.00
-4.50
-4.00
Temperature of Maximum Density. Degrees Centigrade.
0
50
100
150
200
Age In Hours

Fleishman and Wiegner (4) stated that the increase in specific gravity of skimmed milk, milk and cream is due to solidification of fat globules and not to the absorption of gases or molecular changes in milk sugar, and that the change is proportional to the amount of butterfat present. It has been observed that skim milk with very low fat content as determined by Mojonnier increases in density. One explanation was that evaporation of water could cause the increase in density. But from observations on maximum density shifts this possibility is ruled out. When water is added to milk the maximum density shifts toward the maximum density of water, and it is assumed that if water were removed the maximum density would shift to a lower temperature or away from the maximum density of water. This is not detected in the investigation of age versus maximum density, but the tendency is for the maximum to shift toward the maximum density of water, as seen in Plate VII.

SUMMARY

There is no irregularity in the density of milk at the temperature of maximum density of water.

The maximum density of milk was found to be approximately -5.07°C. This maximum shifted toward the maximum density of water when the milk was diluted with water. This shift was proportional to the amount of water added. The maximum density of skim milk was found to be -2.60°C.

The maximum density shifted toward a higher temperature with age, the major portion of this shift coming in the first nine hours after pasteurization.

ACKNOWLEDGMENTS

The author is deeply indebted to Dr. Carrell H. Whitnah, for providing an opportunity to work under him, and for his patience and understanding. Appreciation is given to Dr. H. C. Fryer and Professor Henry Tucker, for their assistance on the statistical analysis of the data. Appreciation is given to Dr. C. F. Oakley for his aid in use of the platinum resistance thermometer. Gratitude is given to my sister Maxine for her patience in typing the thesis.

BIBLIOGRAPHY

(1) Boden, S. M. and C. H. Campbell. "The Estimation of Solids in Milk. Part 1. Determination of Solids-Non-Fat by Various Methods of Hydrometry." J. Dairy Research. 13:45. 1942.

(2) Davies, W. L. The Chemistry of Milk. 2nd ed. New York: Van Nostrand Press, 1939.

(3) Dorsey, N. E. Properties of Ordinary Water Substance. 1st ed. A.C.S. Monograph. New York: Reinhold Publishing Co., 1940.

(4) Fleishman, W. and G. Wiegner. "The Specific Gravity of Cow's Milk and its Change Shortly after Milking." J. Landw. 61:283-324.

(5) Heinemann, B., J. Cosimini, E. L. Jack, J. J. Willingham, and B. M. Zakariasen. "Methods of Determining the Percent Total Solids in Milk by Means of the Lactometer." J. Dairy Sci. 37:869-876. 1954.

(6) Hutchinson, R.C. "The Specific Gravity of Cow's Milk." J. Australian Inst. Agr. Sci. 6:205. 1940.

(7) Olson, T.M. Elements of Dairying. Rev. ed. New York: The McMillan Company. 1950.

(8) Rechnagle, G. "Uber eine Physikallische Eigenschaft der Milch." Milch Ztg. 12:419. 1883.

(9) Rutz, W. D., C. H. Whitnah, and G. D. Baetz. "Some Physical Properties of Milk. I. Density." J. Dairy Sci. 38:1312-1318. 1955.

(10) Sharp, P.H., and R. G. Hart. "The Influence of the Physical State of the Fat on the Calculation of Solids from the Specific Gravity of Milk." J. Dairy Sci. 19:683. 1936.

(11) Weber, Robert L. Heat and Temperature Measurement. New York: Prentice-Hall, Inc. 1950.

(12) Weissberger, Arnold. Technique of Organic Chemistry. Vol. 1. Physical Methods. Part 1. New York: Interscience Publishers, Inc. 1949.

MAXIMUM DENSITY OF MILK

by

THOMAS MILTON MEDVED

B. S., Kansas State College
of Agriculture and Applied Science, 1952

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1956

Densities of homogenized herd milk were measured by the hydrostatic method using an analytical balance and weighted pyrex glass bulbs having approximate diameters and volumes of 28 mm. and 100 ml. respectively. Bath temperatures over the range of -7° to 8°C. were controlled to within 0.001°C. Each sample was placed in a 35 by 250 mm. test tube, and was quickly adjusted to the desired temperature. The volume and rate of expansion of each bulb was determined by weighing it in water at suitable temperatures, and in air of known density.

Irregularities in the density-temperature curve at near 4°C., which were previously reported, were studied with this more precise equipment. They were found to be within the improved experimental error. When milk was supercooled to between -6.25° and -6.75°C., depending on the temperature at which it froze, a maximum density was observed at approximately -5.07°C. The maximum density of milk-water mixtures ranged between -5.17° and 4°C., depending on the percentage of each liquid in the mixture. The maximum density of skim milk was at about -2.60°C.