VIII. LATENT HEAT OF VAPORIZATION

The data on latent heat of vaporization of petroleum oils, given in Table 15, were calculated from the equation

$$L = \frac{1}{d}(110.9 - 0.09t) \tag{6}$$

in which L= latent heat of vaporization in Btu./lb., d= specific gravity of liquid at $60^{\circ}/60^{\circ}$ F., and t= temperature in °F. This equation is based on calorimetric measurements found in the literature on latent heat of vaporization of petroleum distillates, all of which are enumerated briefly in the first part of Table 14.

All of these measurements were made at atmospheric pressure, except for those of Rey, which extended to a pressure of 7 atmospheres. In the experiments of Syniewski, Ormandy and Craven, Regnault, and Kuklin, petroleum vapors were condensed in a water calorimeter. Their results yielded, therefore, values of total heat of vaporization from liquid at room temperature to vapor at 1 atmosphere pressure. These observed values were reduced to latent heats of vaporization for the purpose of comparison (Table 14), by means of the data on specific heat of liquid given in the previous section. The values of latent heat so obtained differ somewhat from those reported by the various authors, because, in one case, an arbitrary value for specific heat was used and, in other cases, the increase of specific heat with temperature was neglected.

Equation (6) is fairly consistent with most of the available experimental data on petroleum distillates as shown by the percentage differences between observed and calculated values. The results obtained by Heinlein are obviously inconsistent with the results of other observers. This was probably caused, in part at least, by the fact that there was good opportunity for reflux condensation in Heinlein's experiments.

Equation (6) yields values which differ less than 10 per cent, on the average, from experimental results obtained at 1 atmosphere pressure on the following hydrocarbons: n-hexane, 4-methylheptane, cyclohexane, and methylcyclohexane (Mathews, J. Am. Chem. Soc., 48, p. 562; 1926); n-hexane, n-heptane, n-octane, hexamethylene, dimethylpentamethylene, methylhexamethylene, and dimethylhexamethylene (Mabery and Goldstein, Proc. Amer. Acad. Arts and Sci., 37, p. 549; 1902); n-decane (Louguinine, Ann. Chim. phys., 13, p. 289; 1898).

In addition to being in general accord with the available experimental results on petroleum distillates and individual petroleum hydrocarbons, equation (6) is in fair agreement with about the only existing evidence on the magnitude of the variation of latent heat with temperature or pressure over a considerable range below the critical point as shown by the second part of Table 14.

There are in the literature numerous values for the latent heat of vaporization of petroleum distillates, some of which were calculated by means of Trouton's rule from measurements of "apparent" molecular weight and "average" boiling point of the distillates, while others were obtained from data on pure substances by means of Trouton's or Hildebrand's rule. The values so obtained are uniformly higher than those found by calorimetric measurements on petroleum distillates, amounting in some cases to nearly 100 per cent. Probably the major reasons for the higher values are (1) that Trouton's and Hildebrand's rules are not applicable to complete vaporization of mixtures with a wide range of boiling points, and (2) that the "apparent" molecular weights of the heavier distillates are too low.

Table 14.—Comparison of observed and calculated values of latent heat of vaporization of petroleum distillates and pure hydrocarbons

Observer					Range				Number of—		Difference in per cent obscalc.			
			Method		Sp. g 60°/60°	Sp. gr. Tem. ° F.		emp.	Oils	Ob- serva- tions	Average		Maxi mum	
Syniewski Gurwitsch Ormandy and Craven_ Leslie, Geniesse, Le- gatski and Jagraw-			Mixtures Not stated Mixtures Electric heating_		. 64-	$egin{array}{ c c c c c c c c c c c c c c c c c c c$		2-470 1-348 2-250 2-576	7 6 3 17	7 6 11 17	_ ±	=2 -4 =4 =6	-6 -9 -10 +10	$\begin{array}{c c} (2) \\ (3) \end{array}$
ski. Regnault Rey Kuklin Redwood Heinlein			Not stated		. 74-	. 81 70-260		1 1 2 4 5	2 6 8 4 23	+ + + +	$\begin{array}{c c} +7 & +1 \\ +9 & +1 \\ +12 & +1 \\ \pm 19 & -3 \\ +40 & +7 \end{array}$		6 (6) (7) (8)	
Tempera	° F.	Pressure atmos.	Laten Observa- tions 10		Difference in per cent obs calc.	Press atm		Obser tions		Calcus Diffe		Differ in p cent cal	obs	Temp.
			(Normal	e)	(Norn			mal hexane)						
20 40 . 60 80	32 68 104 140 176	0. 24 . 55 1. 12 2. 11 3. 60	168 160 152 144 136	171 166 161 156 151	$ \begin{array}{r r} -2 \\ -4 \\ -6 \\ -8 \\ -11 \end{array} $. :	16 36 75	164 158 152 144 146	3	163 158 153 148 143	3	-	-1 -1 -2 -2	0 20 40 60 80
100 120 140 160 180	212 248 284 320 356	5. 80 8. 87 13. 0 18. 5 25. 5	126 116 102 85 63	145 140 135 130 125	$ \begin{array}{r} -15 \\ -21 \\ -32 \\ -53 \\ -98 \end{array} $	3. 9 6. 0 8. 9	2. 42 13 3. 92 12 6. 06 11 8. 94 10 12. 7 9		5	124 -		=	-4 -6 12 19 29	100 120 140 160 180
			(Normal heptane)			(Nor			mal c	octane	e) 	٠		
20 40 60 80	32 68 104 140 176	0. 01. . 05 . 12 . 27 . 56	5 162 158 154 149 143	157 152 148 143 138	+3 +3 +4 +4 +3	. (004 014 04 10 23	16: 150 150 14: 13:	5	153 148 144 139 134	B	4	-5 -5 -4 -4	20 40 60 80
100 120 140 160 180	212 248 284 320 356	1. 05 1. 80 2. 92 4. 54 6. 70	136 129 121 113 105	133 129 124 119 115	+2 0 -2 -5 -9		38	134 129 123 117 110	3	130 125 121 116 112		-	-3 -3 -2 -1	100 120 140 160 180
200 220 240 260 280	392 428 464 500 536	9. 56 13. 3 18. 1 24. 3	96 84 67 39	110 105 100 96	$ \begin{array}{r r} -15 \\ -25 \\ -49 \\ -146 \\ \end{array} $	5. 3 7. 7 10. 8 14. 7 19. 7	73 3 7	10: 94 8: 70 5:	3 .	107 102 98 93 89		_	-6 -9 18 33 75	200 220 240 260 280

¹ Zeitschrift für Angewante Chemie, 11, p. 621; 1898.
2 "Wissenschaftliche Grundlagen der Erdölverarbeitung," 2d ed., p. 144; 1924 (J. Springer, Berlin).
3 J. Inst. Petroleum Technologists, 9, p. 368; 1923.
4 Ind. & Eng. Chem., 18, p. 45; 1926.
5 Mémoires de l'Académie Sciences, France, 26, p. 913; 1862.
6 Annales des Mines, 8, p. 53; 1925.
7 Berichte der Deutschen Chemischen Gesellschaft, 16, p. 949; 1883.
8 "Mineral Oils and Their By-Products" p. 200; 1897 (E. and F. N. Spon (Ltd.), London).
9 Der Motorwagen, p. 395, June 30, 1926.
10 Observed values in Btu./lb. obtained from experimental data on vapor pressure and specific volume by means of Clapeyron equation. (Young, Proc., Royal Dublin Soc., 12, p. 374; 1910; also Mills, J. Am. Chem. Soc., 31, p. 1099; 1909.)

VIII. LATENT HEAT OF VAPORIZATION—Continued

The experimental basis for the data given in Table 15 is described on the preceding pages. The following equation

$$L(\text{Btu./lb.}) = \frac{1}{d} (110.9 - 0.09t)$$

was found to represent satisfactorily most of the experimental results available on petroleum distillates. This equation yields the following convenient relation

$$L(Btu./lb.) \times density (lbs./gal.) = 8.33722 Ld = 925 - 0.75t(Btu./gal.)$$
 (7)

which indicates that the latent heat of vaporization per unit volume of liquid (60° F.) is dependent only on the temperature of vaporization. Thus, the values given in the second column of Table 15 are applicable to any petroleum oil, regardless of gravity. The values given in the other columns are applicable, in general, to all cases of vaporization of petroleum products in which the temperature of vaporization and the gravity of the condensate are known.

The estimated accuracy of the data in Table 15 is 10 per cent, when vaporization occurs at sensibly constant temperature and at pressures below 50 lbs./in.², without chemical change. The tabulated values are probably too low by more than this amount for petroleum products containing large quantities of the lower members of the aromatic series and too high for vaporization at high pressures, as is illustrated in Table 14.

Example 1.—What is the difference between the latent heats of vaporization of a 50° and a 70° A. P. I. gasoline, assuming complete vaporization occurs at 140° F. in the intake system of an internal-combustion engine? According to Table 15, on a weight basis the difference in latent heats amounts to 140-126=14 Btu./lb. or about 10 per cent, while on a volume basis both gasolines require 820 Btu./gal.

Example 2.—How much latent heat is required to vaporize or condense various petroleum products at the average temperatures indicated below?

Product	Gravity,	Average	Latent heat from			
	°A. P. I.	tempera-	Table 15			
	A. P. 1.	ture °F.	Btu./lb.	Btu./gal.		
Gasoline	60	280	116	715		
Naphtha	50	340	103	670		
Kerosene	40	440	86	595		
Fuel oil	30	580	67	490		

Table 15.—Latent heat of vaporization of petroleum oils

Temp. ° F.	Latent heat 10°–80° A. P. I. oils Btu./gal.								
		20	30	40	50	60	70	80	Temp. ° F.
		0.9340	0.8762	0.8251	0.7796	0.7389	0.7022	0.6690	
0 20 40 60 80	925 910 895 880 865				142 140 138 135 133	150 148 145 143 140	158 155 153 150 148	166 163 160 158 155	0 20 40 60 80
100 120 140 160 180	850 835 820 805 790			123 121 119 117 115	131 128 126 124 121	138 135 133 131 128	145 143 140 137 135	152 150 147 144 142	100 120 140 160 180
200 220 240 260 280	775 760 745 730 715		106 104 102 100 98	113 110 108 106 104	119 117 115 112 110	126 123 121 118 116	132 130 127 125 122	139	200 220 240 260 280
300 320 340 360 380	700 685 670 655 640	90 88 86 84 82	96 94 92 90 88	102 99 97 95 93	108 105 103 101 98	113 111 109 106 104	119		300 320 340 360 380
400 420 440 460 480	625 610 595 580 565	80 78 76 74 73	85 83 81 79 77	91 89 86 84 82	96 94 91 89 87	101			400 420 440 460 480
500 520 54 0 560 580	550 535 520 505 490	71 69 67 65 63	75 73 71 69 67	80 78 75 73 71	85				
600 620 640 660 680	475 460 445 430 415	61 59 57 55 53	65 63 61 59 57	69					
700 720 740 760 780	400 385 370 355 340	51 49 47 45 44	55 53 51 48 46						
800	325	42	44						