CALCULATING SOME OF THE OPTICAL CHARACTERISTICS OF ELEMENTS AND COMPOUNDS FROM THEIR PHASE TRANSITION TEMPERATURES AT A PRESSURE OF 101.325 kPa (760 mm Hg). II.

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A method of choosing a spectral region for the identification of materials and improving phase transition temperatures is proposed.

Studies of the spectra of materials in the ultraviolet and visible regions have allowed us to obtain a deeper understanding of the structure and interaction of materials on the atomic level, and the results have found numerous practical applications [1]. The infrared region of the spectrum, which allows one to observe the structure and composition of molecules, has come to be more intensely exploited and used in recent decades, and is also finding more and more practical applications [2]. However, one of the substantial drawbacks of spectral methods is the abundance of information contained in spectra and the consequent difficulty of interpreting them. And, even if there are a sufficient number of reference points (lines) in the spectrum which can be uniquely explained and interpreted, the situation is more complex in the infrared from both the experimental and theoretical point of view. As was pointed out in [2], molecular spectra are of interest for the determination of thermodynamic parameters, and successfully solving the materials identification problem frequently depends on what region of the spectrum is chosen for this.

In [3], it was shown that the heat of vaporization and heat of fusion can be calculated given information on the melting and boiling points at a pressure of 101.325 kPa. Using the ideas and assumptions used in [3] to derive theoretical relations for determining the heats of phase transitions, we obtained expressions for determining the positions of the absorption maxima for elements and compounds; these expressions may be used in choosing a region of the spectrum for identifying materials and improving their thermodynamic properties. The following equations were obtained for calculating the positions of the absorption maxima for a material with melting point T_m and boiling point T_b:

$$\lambda_1 = \frac{2898}{T_m}, \tag{1}$$

$$\lambda_2 = \frac{2898}{T_b}. \tag{2}$$

We shall now compare the calculated [using (1) and (2)] and experimental (the closest values in [4] to the calculated positions) positions of the corresponding absorption maxima for the elements in the periodic table. The values calculated from (1) and (2) are on the first line in the column opposite the name of the element (see Table 1), and the values closest to them from [4] are in the second line.

As follows from Table 1, the positions of the absorption bands determined from (1) and (2) and those determined experimentally do not differ significantly in most cases; there are, however, physical reasons for this. Thus, the element beryllium has a melting point of 1283 °C in [5], where the values of T_m and T_b were obtained, while a value of 1285°C is given in [6]; this yields 1.8623 and 1.8599 μm, respectively, for λ. Thus, the calculated position of the line with maximum absorption is very sensitive to the error in the temperature measurement. A 2° error in the temperature measurement at a temperature of 1556°K shifts the corresponding maximum by 24 Å. And, if it is assumed that the position of the experimental 1.8413 μm line (the value closest to that calculated from the melting point, which was determined with some error) in fact corresponds to the melting point, we can then calculate the melting

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TABLE 1. Emission Wavelengths (calculated and experimental) of the Elements

Element	λ₁	λ₂	Element	λ₁	λ₂
H_2	193,846	142,126	H	—	—
	—	—		—	—
Li	6,388	1,8225	F	52,5475	34,074
	—	1,8697		—	—
Na	7,811	2,4915	Cl	16,8341	12,1184
	—	2,3379		—	—
K	8,61	2,8219	Br	10,9	7,746
	8,51	2,7215		—	—
Rb	2,292	2,974	I	7,4932	6,3559
	—	2,790		—	—
Cs	9,6027	3,024	At	5,0562	4,4574
	—	3,010		—	—
Be	1,862	1,0537	O_2	53,33	32,1464
	1,8144	1,0119		—	—
Mg	3,1409	2,0801	S	7,4627	4,0376
	—	—		—	—
Ca	2,5802	1,6463	Se	6,0305	3,1156
	2,1428	1,6195		—	—
Sr	2,7781	1,7669	Te	4,0102	2,2946
	2,7355	2,0262		—	—
Ba	2,9476	1,5171	Po	2,3615	2,3462
	2,9223	1,5000		—	—
Ra	2,9779	1,6018			
	—	—			
Sc	1,7320	0,6944	N	45,8616	37,4466
	—	—		—	—
Y	1,6343	0,8344	P	—	—
	—	0,8800		—	—
La	2,4288	0,7954	As	10,8458	8,7513
	—	0,8001		—	—
Ac	1,9712	0,8049	Sb	3,2087	1,5171
	—	0,7886		—	—
Ti	—	—	Bi	5,3228	1,5817
				—	—
Zr	1,4929	0,8156	C	—	—
	—	0,7979		—	—
Hf	1,3617	0,6228	Si	1,7085	1,1026
	—	0,6267		1,7327	1,1017
Ku	1,1717	0,5294	Ge	2,3943	0,9338
	—	0,5294		—	0,9398
	—	—	Sn	5,7369	0,979
	—	—		—	0,9742
	—	—		—	1,3102
V	1,4467	0,7932	B	1,2582	0,6944
	—	0,7937		—	0,6081
Nb	1,0499	0,5602	Al	3,1052	1,0653
	1,0419	0,5642		—	1,0768
Ta	0,8864	0,5108	Ga	9,5665	1,1591
	0,8447	0,5109		—	1,1949
	—	—	In	7,4932	6,3559
				—	—
	—	—	Tl	5,0255	1,6749
				5,1058	1,6340
Cr	1,3317	0,9941	Zn	4,1839	2,4766
	—	1,0080		—	—
Mo	0,9999	0,5712	Cd	4,8773	2,7915
	—	0,5722		—	—
W	0,7932	0,4993	Hg	12,3692	4,6008
	0,7940	0,4994		—	4,5122
Mn	1,9101	1,2237	Cu	2,3025	1,0104
	—	1,2899		—	1,0146
Tc	1,2009	0,5827	Ag	2,3485	1,1601
	—	0,5836		—	1,2551
Re	0,8392	0,4934	Au	2,1689	0,9772
	0,8357	0,4924		—	0,9391
Fe	1,6027	—	Ni	1,6788	0,9430
	—	—		1,6868	0,9396
Ru	1,0450	0,6611	Pd	1,5878	0,7560
	—	0,6663		—	0,7486
Os	0,9747	—	Pt	1,4190	0,6323
	—	—		—	0,6326
He	840	556	Co	1,6417	1,1462
	—			—	1,1318
Ne	113,4246	106,9372	Rh	1,2977	0,6845
	—	—		—	0,6965
Ar	34,5617	33,2034	Ir	1,0669	0,6268
	—	—		—	0,6830
Kr	24,9935	24,1600		—	—
	—	—			
Xe	17,972	17,5583		—	—
	—	—			
Rn	14,3358	13,7248		—	—
	—	—			

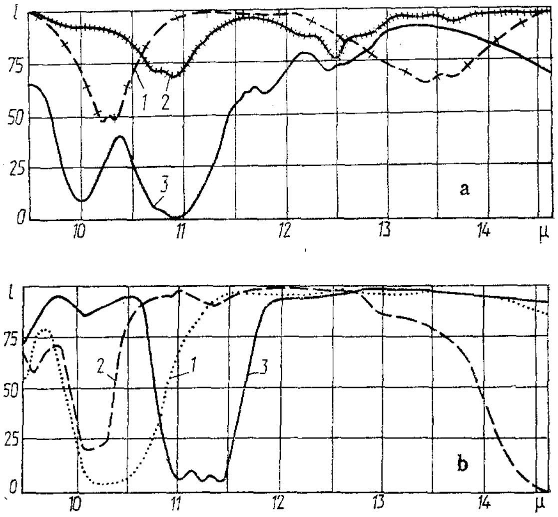

Fig. 1. Theoretical (a) and experimental (b) spectral transmission curves. a: 1) n-Butane; 2) isobutane; 3) 1-butene. b: 1) trans-Butene; 2) cis-cutene; 3) isobutene.

point, and we obtaim $T_m = 1324°C$ and $T_b = 2590°C$ for Be. Thus, the method discussed above can be used to improve melting and boiling points: we determine the appropriate temperatures by the well-known methods (determining absolute temperatures and estimating the errors in the temperature determination present great difficulties), calculate λ_1 and λ_2 from (1) and (2), and search for the nearest experimental absorption band values, and immediately obtain values for T_m and T_b. As follows from Table 1, the smallest differences between the experimental and calculated λ occur for the elements Cu, Ni, Al, Rd, and Pt in materials used in thermocouples, i.e., for temperature determination.

The great sensitivity of the position of maximum absorption to melting and boiling points may also be used for identifying materials and compounds (in particular, isomers). It is advisable to use the spectral region $\lambda_2 - \delta < \lambda < \lambda_1 + \delta$ (which, for the majority of organic compounds, requires the use of the infrared region of the spectrum) for identification.

Absorption spectra for n-butane and its isomers and derivatives: n-butane ($T_m = 135.35$ °C, $T_b = 0.50°C$), isobutane ($T_m = 159.60°C$, $T_b = -11.7°C$), 1-butene ($T_m = 185.3°C$, $T_b = -6.25$ °C), cis-2-butene ($T_m = -138.91°C$, $T_b = 3.72°C$), and trans-2-butene ($T_m = -105.65°C$, $T_b = 0.88°C$).

The values of λ_1 and λ_2 calculated from (1) and (2) are: n-butane – $\lambda_1 = 21.4985, \lambda_2 = 10.629$; isobutane – $\lambda_1 = 25.5217$, $\lambda_2 = 17.9498$; 1-butene – $\lambda_1 = 32.998$, $\lambda_2 = 10.8579$; cis-2-butene – $\lambda_1 = 21.5882$, $\lambda_2 = 10.10467$; and trans-2-butene – $\lambda_1 = 17.2911$, $\lambda_2 = 10.5754$.

By comparing the theoretical and experimental data (see Fig. 1) on the absorption peaks (we were not able to find the long-wavelength region of the spectra of these compounds; for that reason, they are not presented here), we see that they are in satisfactory agreement with one another, and can be used for identification.

It would be of great interest to obtain experimental absorption spectra for the elements in the periodic table in the region $\lambda = n\lambda_1$, where n is the number of the element group from [3] used in determining the heat of fusion.

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