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PHASE TRANSITIONS IN ELEMENTS AND COMPOUNDS. PART 3

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There is shown to be good agreement for certain systems between the optical and thermodynamic parameters characterizing collective phenomena: laser emission and phase transition.

Thermodynamics arose from practical heat engineering (macroscopic thermophysics) and has since been extended to all known physical, chemical, and biological phenomena and has thus had a substantial effect on many disciplines. The role of thermodynamics in science is evident from the general use of concepts such as temperature, energy, and entropy. As thermodynamics is a phenomenological discipline, it influences thermophysics at the macroscopic level. Although advances in thermodynamics were stimulated originally by heat engineering, the subject has had a large effect not so much on the latter but on disciplines concerned with phenomena at the microscopic level. Statistical mechanics enables one to relate phenomena observed at the microscopic level to general measured macroscopic parameters.

A major task in thermophysics, the theory of elasticity, hydrodynamics, and so on is to establish relationships between the macroscopic parameters (observed ones) and the microscopic ones. Difficulties arise here both because of the complexity of the phenomena (these being determined by several forms of interaction) and also in difficulties in obtaining information on the elementary steps giving rise to the observed macroscopic parameters. Phenomena determined by single forms of interaction have usually been thoroughly researched, and such simple phenomena include laser emission. In research on complicated processes such as for example phase transitions, it is desirable to establish the roles of simpler phenomena.

In that respect, considerable interest attaches to processes responsible for phase transitions, which may be compared with the collective phenomena determining lasing. It has been shown [1, 2] that quantities such as the latent heats of phase transitions and the positions of peaks in absorption spectra are related to phase-transition temperatures under normal conditions via Wien's displacement law.

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TABLE 1. Comparison of Laser Wavelengths Calculated from (1) and (2) with Measurements

Element or substance	T_{mp}	T_{bp}	λ_1	λ_2	λ_1'	λ_2'
Ne	25,55	27,1	113,43	106,94	124,52	106,07
Xe	161,25	165,05	17,972	17,558	—	18,506
HCl	158,95	187,95	18,23	15,41	18,522	16,21
HF	189,79	292,61	15,01	9,9	15,26	10,19
H_2O	273,15	373,15	10,61	7,77	11,83	7,71
NH_3	195,42	239,74	14,82	12,08	14,78	—

Here we direct attention to the correlation between certain lasing-transition wavelengths and the wavelengths corresponding to absorption peaks defined by phase-transition temperatures under normal conditions. The peak positions [2] are given by

$$\lambda_1 = \frac{2898}{T_{mp}}, \quad (1) \qquad \lambda_2 = \frac{2898}{T_{bp}}. \quad (2)$$

In [3], wavelengths are given for lines in air for laser transitions, which are compared with those calculated from (1) and (2) for various substances (Table 1).

The values calculated from (1) and (2) virtually coincide with the measured ones; if one uses the group feature n introduced in [1], one obtains a satisfactory correlation for numerous transitions. It is evident that the interactions play an important part here, since there are parameters characterizing the elementary acts in lasing and in phase transitions, from which it is possible to calculate the transitions [1] and derive details of the absorption spectra [2].

This correlation is of considerable practical and theoretical interest in relation to recording absorption and emission spectra accompanying melting, boiling, crystallization in supercooled liquids and supersaturated solutions, and detonation in the wavelength range defined by (1) and (2) from the transition temperatures at normal pressure. Considerable interest also attaches to the emission and absorption spectra for the vapors of metals used in thermocouples near temperatures where the emf changes sign and in the wavelength range defined by (1) and (2) at the temperature defined by the sign change.

NOTATION

T_{mp}, T_{bp}, melting and boiling temperatures under normal conditions; λ_1, λ_2, wavelengths (μm) given by (1) and (2), respectively; λ_1', λ_2', wavelengths of laser transitions nearest to the calculated values (taken from [3]).

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