THERMOELECTRIC METHOD OF DETERMINING THE THERMAL CONDUCTIVITY OF GASES AND LIQUIDS. INVESTIGATION OF THE THERMAL CONDUCTIVITY OF ACETIC ACID VAPORS

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A thermoelectric method of determining the thermal conductivity of gases and liquids is described based on using the Peltier effect. Data are presented on the thermal conductivity of neon, PMFS-4, and acetic acid vapors.

Sufficiently rigid requirements relative to the working temperature difference in the measuring cell are imposed on experimental methods used in investigating the thermal conductivity of gases and liquids at high pressures, at the critical isochore, and near the critical point. The probability of convection occurring limits this difference to ones and, from time to time, to fractions of a degree. The temperature drop in the investigation of the thermal conductivity of chemically reacting gases is constrained by the uncertainty in the composition of the substance being investigated.

Under these conditions the known stationary methods of measuring the thermal conductivity become unreliable, since the error in the experiment grows sharply with the decrease in q and Δt in an independent determination of the heat flux and temperature difference. A reduction in the error of measuring q and Δt is fraught with considerable difficulties and most often does not yield the desired effect. The requirements on the method of determining the thermal conductivity for small temperature drops can be reduced to the following.

1) The heat source and the temperature-difference sensor should be common in principle. Only in this case can the condition $\Delta t \rightarrow 0$ as $q \rightarrow 0$ be assured.

2) The influence of thermostating on the measurement of the temperature difference should be reduced to the limit.

The thermoelectric stationary method of determining the thermal conductivity of gases and liquids on the basis of using the Peltier effect, proposed by Professor D. L. Timrot and described in this paper, approximates these requirements.

THERMOELECTRIC METHOD OF DETERMINING THE THERMAL CONDUCTIVITY

A thermoelectric loop (Fig. 1), consisting in the simplest case of two junctions and placed in an isothermal medium, can be arranged so that the temperature difference between the junctions, occurring during passage of electrical current from an external source over the loop, is determined mainly by either the thermal conductivity of the loop materials or by heat exchange with the environment. If the environment is fixed, the temperature difference between the junctions in this latter case is easily related to the thermal conductivity of this medium.

As is known, the mentioned thermoelectric method has already been used in a number of papers [1,2] to measure the thermal conductivity of metals and semiconductors. Insofar as the authors know, this is the first time the method is being used to investigate gases and liquids.
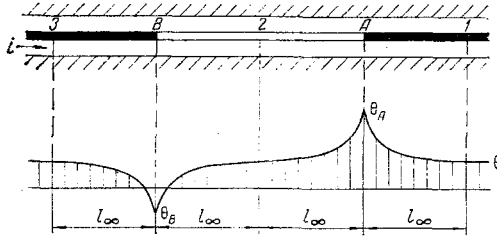

Fig. 1

Fig. 2

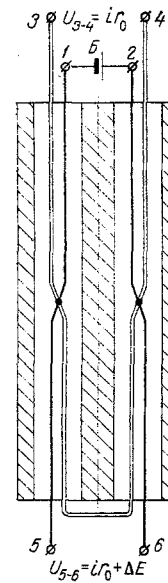Fig. 1. Temperature distribution in a two-junction differential thermocouple during current passage.

Fig. 2. Diagram of a double thermocross.

The thermoelectric loop can be realized in the form of a wire differential thermocouple in determining the thermal conductivity of gases and liquids not too close to the critical value; convection is eliminated by diminishing the temperature difference between the junctions.

The heat-balance equation for one of the conductors (1-A, A-2, 2-B, B-3) is written as

$$S_M \lambda_M \frac{d^2\theta}{dx^2} = \left\{ \frac{2\pi\lambda \, gas}{\ln D/d} + 4\sigma_0 \varepsilon_M \pi d T_0^3 \right\} \theta - \frac{\rho_M i^2}{S_M}. \tag{1}$$

Let us introduce the following boundary conditions:

$$\text{for} \quad x = l_\infty, \quad \theta = t - t_0 = 0;$$

$$\text{for} \quad x = 0, \quad \theta = \theta_{A,B}; \quad \pm\Pi i = \Sigma - S_M \lambda_M \left(\frac{d\theta}{dx} \right)_{x=0}. \tag{2}$$

Taking account of the first boundary condition (for x = L∞, θ = 0) and the first part of the second boundary condition (for x = 0, $\theta = \theta_{A,B}$), the solution of (1) will be

$$\theta = -\left\{ \frac{\frac{g}{m^2} + \left(\theta_{A,B} - \frac{g}{m^2} \right) e^{-ml_\infty}}{2 \coth m l_\infty} \right\} e^{mx} + \left\{ \frac{\frac{g}{m^2} + \left(\theta_{A,B} - \frac{g}{m^2} \right) e^{ml_\infty}}{2 \sinh m l_\infty} \right\} e^{-mx}, \tag{3}$$

where

$$m^2 = \left\{ \frac{2\pi\lambda \, gas}{S_M \lambda_M \ln D/d} + \frac{4\sigma_0 \varepsilon_M \pi d T_0^3}{S_M \lambda_M} \right\}; \quad g = \frac{\rho_M i^2}{S_M^2 \lambda_M},$$

with the subscripts corresponding to the conductors being considered.

It follows from the boundary conditions (2) that $\coth m l_\infty \to 1$ and $\sinh m l_\infty \to \infty$. Taking this fact into account, using the second part of the boundary conditions (2) and (3), we can write that the temperature at the junctions θ_A and θ_B equals

$$\theta_{A,B} = \frac{\pm\Pi i + \left(\frac{\rho_1}{S_1 m_1} + \frac{\rho_2}{S_2 m_2} \right) i^2}{S_1 \lambda_1 m_1 + S_2 \lambda_2 m_2}. \tag{4}$$

while the temperature difference between the junctions ($t_A - t_B$) is

TABLE 1. Dependences of θ_A, θ_B, and $(t_A - t_B)$ on Magnitudes of the Working Current i

i, mA	U_{5-6}, mV	U_{3-4}, mV	ΔU, mV	i, mA	Δe_A, mV	$-\Delta e_B$, mV	Δe_{A-B}, mV
Argon, $t_0 = 88,4$ °C							
15,0933	33,5257	33,4493	0,0764	15,0753	0,0437	0,0326	0,0763
12,1299	26,9407	26,8796	0,0611	12,1152	0,0345	0,0270	0,0615
9,0736	20,1575	20,1116	0,0459	9,0633	0,0249	0,207	0,0456
6,0345	13,4058	13,3750	0,0308	6,0277	0,0162	0,0140	0,0302
2,9691	6,5950	6,5798	0,0152	3,0495	0,0081	0,0075	0,0156
Argon, $t_0 = 0$ °C							
15,1857	33,7683	33,7125	0,0558	15,0631	0,0327	0,0211	0,0538
12,1723	27,0672	27,0221	0,0451	12,0910	0,0253	0,0178	0,0431
9,0817	20,1972	20,1630	0,0342	9,0345	0,0182	0,0139	0,0321
6,1275	13,6269	13,6036	0,0233	6,0013	0,0116	0,0096	0,0212
3,0657	6,8178	6,8055	0,0123	3,0321	0,0056	0,0051	0,0107

$$(t_A - t_B) = \frac{2\Pi i}{(\sqrt{\lambda_1 S_1} + \sqrt{\lambda_2 S_2})} \left(\frac{2\pi\lambda \text{ gas}}{\ln D/d} + 4\sigma_0 \varepsilon_{av} \pi d T_0^3 \right)^{-0.5}, \tag{5}$$

where D and d are the diameters of a cylinder and a conductor, respectively; λ and S are the coefficient of thermal conductivity and the section of the appropriate electrode of the differential thermocouple; and ρ is the specific resistivity of the differential thermocouple electrodes.

It was assumed in deriving (5) that $\varepsilon_1 = \varepsilon_2 = \varepsilon_{av}$. This can be realized by selecting appropriate materials for the differential thermocouple electrodes or by finding ε_{av} experimentally from vacuum tests.

It follows from (4) and (5) that the temperature of each junction is a function of the Peltier coefficient and the Joule heat; the temperature difference between the junctions is proportional to the working current (and, therefore, is independent of the Joulean heat), and the thermostat temperature does not enter explicitly into (5).

Therefore, upon compliance with the identical conditions of heat exchange between the junctions and the environment, and within the limits of constancy of the physical parameters, the thermostat temperature fluctuations have practically no effect on the measurements of the temperature difference between the junctions.

MEASUREMENT DIAGRAMS. A. DOUBLE THERMOCROSS

The diagram (Fig. 2) permits the measurement of both the temperature difference between the junctions and the temperature of a junction individually. The dependences of θ_A, θ_B, and $(t_A - t_B)$ on the magnitude of the working current i, obtained in an argon medium, are represented in Table 1. It is seen that (4) and (5) are verified well experimentally. It is also seen from Table 1 that the sufficiently noticeable spread in the values of θ_A and θ_B around the averaging curves vanishes completely in the case of measuring the difference $(t_A - t_B)$, as also follows from (5).

Inserting the quantities to be measured, i.e., $\Pi_0 = T_0 (dE/dT)_{T_0}$ and $(t_A - t_B) = (E_A - E_B)/(dE/dT)_{T_0}$, directly into (5) and taking into account that $(t_A - t_B) \ll T_0$, we obtain

$$\frac{(E_A - E_B)}{i} = \frac{1}{2} \cdot \frac{2T_0 \left(\dfrac{dE}{dT} \right)_{T_0}^2}{(\sqrt{\lambda_1 S_1} + \sqrt{\lambda_2 S_2})} \left(\frac{2\pi\lambda \text{gas}}{\ln D/d} + 4\sigma_0 \varepsilon_{av} \pi d T_0^3 \right)^{-0.5} \tag{6}$$

The factor $1/2$ accounts for the fact that heat exchange with the environment is experienced by twice as many conductors in the thermocross configuration as compared with Fig. 1. Experimental dependences $\Delta E / i(\lambda_{gas}^{-0.5})$, obtained at several isotherms for air, neon, and helium, are presented in Fig. 3. The slopes of the lines in Fig. 3 are characterized by the quantity

$$K(t) = \frac{2T_0 \left(\dfrac{dE}{dT} \right)_{T_0}^2}{(\sqrt{\lambda_1 S_1} + \sqrt{\lambda_2 S_2})}, \tag{7}$$

which is a temperature-dependent constant of the instrument.

Fig. 3.
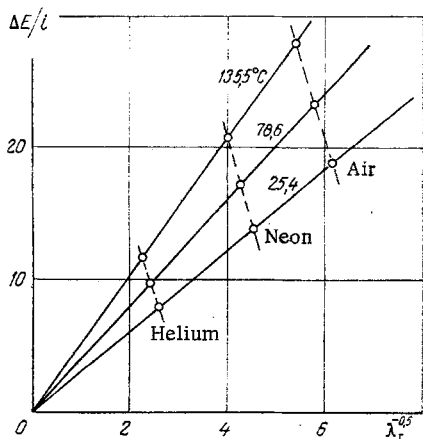

Fig. 4.

Fig. 3. Ratio $\Delta E/i$, μ V/mA, versus $\lambda_{gas}^{-0.5}$, showing temperature variation of the instrument constant K(t).
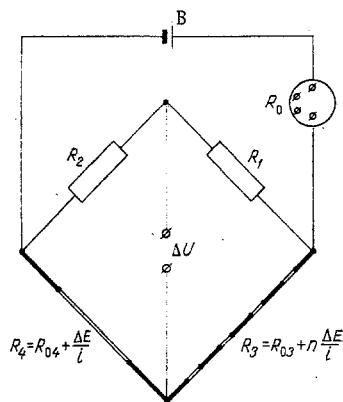
Fig. 4. 2n-junction bridge circuit.

The method described can be used in absolute and relative variations. The absolute variation, which can be realized in principle, indubitably submits to the relative variation, since the latter does not require knowledge of dE/dT and λ of the differential thermocouple materials.

Measurements by the double thermocross diagram are associated with determining a small difference between two large quantities, which is not desirable (see Table 1). Hence, the tendency to increase the quantity being measured ΔE, and, moreover, to obtain it directly, is natural. The 2n-junction bridge circuit developed by the authors (Fig. 4) corresponds to this.

MEASUREMENT DIAGRAMS. B. 2n-JUNCTION BRIDGE CIRCUIT

The arm R_3 of the circuit in Fig. 4 is a 2n-junction differential thermocouple. The arm R_4 is a 2-junction thermocouple fabricated from the same materials as R_3. The magnitude of the bridge unbalance when a current i passes through the junction will be

$$\frac{\Delta U}{i} = (n-1) \frac{T_0 \left(\frac{dE}{dT} \right)_{T_0}^2}{(\sqrt{\lambda_1 S_1} + \sqrt{\lambda_2 S_2})} \left(\frac{2\pi\lambda\, gas}{\ln D/d} + 4\sigma_0 \varepsilon_{av} \pi d T_0^3 \right)^{-0.5} + \frac{(R_{03} - R_{04})}{2}, \qquad (8)$$

where $(R_{03} - R_{04})/2$ is the shift of the reference zero in the diagram in Fig. 3 and can be reduced to a negligibly small quantity by selecting the resistances of the differential thermocouple branches.

The variations of measurement bridge circuits are evidently not exhausted by the circuit in Fig. 4 and can be altered in conformity with the requirements of experiment.

In a relative variation of the method, the process of thermal-conductivity measurement is especially simple and reduces to the following.

TABLE 2. Experimental Results on the Thermal Conductivities of Neon and the Fluid PMFS-4

t, °C	λ, W/m·°K	$\frac{\lambda - \lambda_T}{\lambda_T}$, %	t, °C	λ, W/m·°K	$\frac{\lambda - \lambda_T}{\lambda_T}$, %
Neon			PMFS-4		
0	,04600	+0,55	0	,1490	—0,8
15,6	,04772	+0,25	0	,1477	—1,67
			17,9	,1457	—1,62
29,9	,04985	+1,14	30,1	,1482	+1,0
			34,8	,1462	0
44,7	,05120	+0,55	45,2	,1473	+1,58
60,0	,05314	+0,88	51,0	,1483	+2,85
			65,6	,1433	+0,50
75,1	,05513	+1,33	70,3	,1448	+1,90
			79,0	,1444	+2,40
95,8	,05721	+0,81	93,8	,1437	+3,15
			94,9	,1440	3,45

TABLE 3. Experimental Results on the Thermal Conductivity of Acetic Acid Vapors

Isotherm 25.4°C

P, mm Hg	λ_{exp}, W/m·°K	λ_{true}, W/m·°K
3,5	,06704	,06934
4,8	,05955	,06104
6,0	,05454	,05563
7,8	,04816	,C4890
10,6	,04272	,04320
13,2	,03902	,03938

Isotherm 39.5°C

P, mm Hg	λ_{exp}, W/m·°K	λ_{true}, W/m·°K
10,6	,06274	,06345
12,7	,05862	,05917
16,7	,05306	,05344
19,6	,04962	,04992
27,6	,04367	,04386

Isotherm 55.0°C

P, mm Hg	λ_{exp}, W/m·°K	λ_{true}, W/m·°K
3,5	,06831	,07065
6,3	,07019	,08172
6,8	,08130	,08274
7,6	,08244	,08374
8,5	,08338	,08466
9,2	,08348	,08457
10,0	,08224	,08323
11,5	,08048	,08132
15,4	,07524	,07582
19,6	,06991	,07034
24,8	,06517	,06549
31,2	,06060	,06083
50,6	,05182	,05194

Isotherm 64.3°C

P, mm Hg	λ_{exp}, W/m·°K	λ_{true}, W/m·°K
7,2	,07793	,08010
8,8	,08433	,08625
9,8	,08434	,08606
10,3	,08476	,08641
11,0	,08436	,08589
11,5	,08442	,08589
12,8	,09379	,08510
15,0	,08286	,08397
19,2	,07929	,08012
19,4	,07923	,08005
19,5	,07909	,07990
24,8	,07490	,07550
30,7	,07132	,07178
30,9	,07077	,07123
49,6	,06217	,06242

Isotherm 64.3°C

P, mm Hg	λ_{exp}, W/m·°K	λ_{true}, W/m·°K
49,8	,06231	,06256
50,4	,06213	,06238
76,0	,05487	,05501

Isotherm 78.6°C

P, mm Hg	λ_{exp}, W/m·°K	λ_{true}, W/m·°K
3,5	,03558	,03898
6,7	,05389	,05658
7,5	,06064	,06334
49,2	,06142	,06252
77,5	,06964	,07034
115,0	,07560	,07615
167,0	,07799	,07830
235,0	,07820	,07848
302,0	,07621	,07643

Isotherm 135.5°C

P, mm Hg	λ_{exp}, W/m·°K	λ_{true}, W/m·°K
8,2	,03257	,03846
18,4	,03716	,04016

(continuation)

P, mm Hg	λ_{exp}, W/m·°K	λ_{true}, W/m·°K
9,1	,06740	,06988
9,2	,06773	,07019
11,6	,07496	,07712
11,9	,07503	,07714
14,9	,07941	,08119
17,6	,08166	,08321
20,2	,08264	,08401
20,2	,08269	,08406
23,8	,08309	,08426
24,4	,08289	,08403
28,0	,08366	,08366
32,2	,08207	,08292
33,4	,08132	,08213
41,4	,07969	,08033
47,8	,07761	,07815
50,4	,07697	,07748
64,5	,07319	,07357
74,5	,07055	,07087
81,0	,06940	06969
101,0	,06527	,06549
111,0	,06347	,06366
121,0	,06183	,06200
143,0	,05894	,05908
161,0	,05658	,05670

Isotherm 93.1°C

P, mm Hg	λ_{exp}, W/m·°K	λ_{true}, W/m·°K
7,2	,04187	,04482
11,6	,05533	,05775
12,0	,05655	,05905
13,0	,06682	,06870
18,4	,06783	,06970
31,4	,07744	,07869
31,8	,07737	,07860
39,4	,07952	,08054
45,4	,08000	,08089
47,0	,08026	,08112
50,4	,08048	,08129
54,0	,08047	,08123
59,0	,07985	,08054
62,0	,08008	,08073
64,0	,07999	,08062
74,0	,07916	,07970
84,0	,07759	,07806
95,0	,07696	,07737
115,0	,07406	,07439
116,0	,07470	,07503
122,5	,07317	,07347
141,0	,07197	,07223
181,0	,06737	,06756
182,0	,06664	,06683
199,0	,06690	,06707
225,0	,06489	,06504
243,0	,06386	,06399
261,0	,06348	,06360

Isotherm 110.6°C

P, mm Hg	λ_{exp}, W/m·°K	λ_{true}, W/m·°K
6,0	,02706	0,3095
11,5	,03349	0,3600
19,0	,04154	0,4343
30,0	,05096	,05240
30,5	,03983	,04177
48,4	,04413	,C4549
78,0	,05075	,05172
112,0	,05736	,05912
163,0	,06427	,06486
232,0	,06994	,07039
287,0	,07290	,07328

1. The dependence $\Delta U/i(\lambda_{eff}^{-0.5})$ is recorded on an isotherm for two calibrating gases (Fig. 3). Then $K(t_0)$ and $(R_{03}-R_{04})/2$ are determined from these data.

2. Repetition of the above first step for several isotherms yields the temperature dependence of $K(t)$.

3. The coefficient of thermal conductivity of the substance being investigated is computed by means of the $\Delta E_x/i$ and $K(t)$ measured for it.

The working differential thermocouple in an apparatus operating according to the circuit in Fig. 4 was fabricated from $\varnothing$ 0.2 Chromel and Constantan and had nine pairs of junctions. The calibration was made in air and helium.

The thermal conductivities of neon and a PMFS-4 fluid were measured on this apparatus in a 0–96°C temperature range P at 1 = atm (Table 2). A comparison with handbook data [3] shows that the results agree within the error limits of the present experiment and the data of [3]. This indicates the accuracy and stability of the method.

INVESTIGATION OF THE THERMAL CONDUCTIVITY
OF ACETIC ACID VAPORS

The thermal conductivity of acetic acid vapors (CH_3COOH) as a function of the temperature and pressure was measured on this same apparatus. The selection of the CH_3COOH vapors as the substance to be investigated was because the CH_3COOH molecules form dimers on a hydrogen–bond base, exactly as do other carboxylic acids. The large magnitude of the hydrogen–bond energy ($\Delta H_{CH_3COOH} \approx 14$ kcal/mole) and the possibility of experimental realization of the parameters for which the composition varies from $\alpha \approx 1$ to $\alpha \approx 0$ makes carboxylic acids convenient model substances for the clarification of the regularities of the dimerization reaction.

The dimerization reaction rate in carboxylic acid vapors is sufficiently high and permits the assumption that local thermochemical equilibrium holds in the gas under investigation. It hence follows that the experimental results on the thermal conductivity of CH_3COOH vapors can be described by dependences obtained for reacting gases with a high reaction rate. Moreover, the viscosity of carboxylic acid vapors has been studied well at this time, which permits a comparison of the appropriate interaction parameters computed from experimental results on λ and η.

Acetic acid, first checked for the moisture content, was poured into the evaporation tank of the apparatus in the amount of ~2.5 cm³. The acetic acid was frozen by liquid nitrogen before the measurements and the incident air was removed from the apparatus. The thermal conductivity of the acetic acid vapors was measured on the isotherms at pressures from 3.5 mm Hg, corresponding to the temperature of melting ice, to the saturation line at T_0. The measurement results for eight isotherms are presented in Table 3.

In the case of carboxylic acid vapors, exactly as in the determination of the thermal conductivity of gases, a correction for the temperature jump on the gas—solid interface must be inserted at low pressures. At low pressures, where this correction is large, the monomer content in the mixture approaches 100% and the temperature jump can hence be computed from appropriate experimental results by the usual means, i.e., without taking account of the influence of the dimerization reaction. Values of the thermal conductivity corrected for the temperature jump are presented in Table 3.

The behavior of the thermal conductivity in the $\lambda_T(P)$ diagram is characteristic for the thermal conductivity of chemically reacting gas mixtures. The location of the thermal-conductivity "peaks" corresponds to a vapor composition with $\alpha \approx 0.5$, computed according to the hydrogen-bond energy.

On the basis of the experimental data obtained for the thermal conductivity, it is later assumed that the magnitude of the hydrogen-bond energy and, therefore, the vapor composition as a function of the pressure and temperature can be refined, and the interaction section of different kinds can also be computed.

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