

gree of temperature. For some couples H is practically a linear function of t over considerable ranges of temperatures, i.e., $H = a + bt$ and is a measure of the sensibility of any type of couple. We may cite the following as illustrations:

THERMOELECTRIC POWERS OF THERMOCOUPLES.

Thermocouple.	Thermoelectric power (microvolts).	Temperature range.	Author.
Pt, 90 Pt - 10 Rh	$4.3 + 0.0088 t$	0-1300	Le Chatelier
Pt, 90 Pt - 10 Ir	$11.3 + 0.0104 t$	0-1000	Le Chatelier
Pt, Ni	$7.8 + 0.01325 t$	300-1300	Burgess
Cu, Ni	$24.4 + 0.016 t$	0-235	Pécheux
Cu, Constantan	$42.3 + 0.058 t$	0-320	Pécheux
Pt - Fe (forged)	$2.5 + 0.0210 t$	700-1000	Le Chatelier

It is usual to express H for a single substance in terms of lead as a standard at ordinary temperatures, but at high temperatures this becomes impracticable. The values of H for steels are of special interest in view of their use in many base-metal

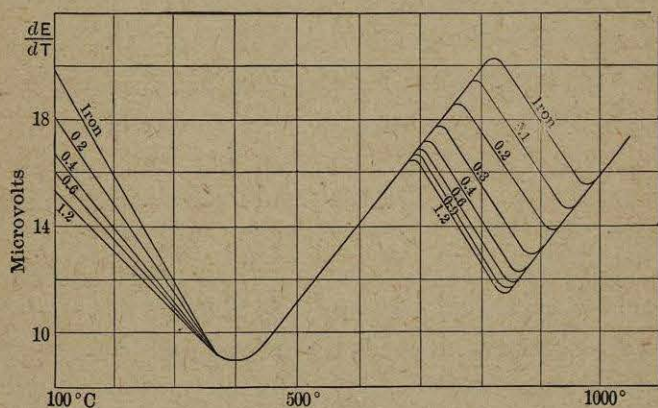


Fig. 23. Thermoelectricity of Steels.

couples. In Fig. 23, due to Belloc, are given the changes of H , with temperature and carbon content for various steels against Pt, from which it is evident that thermocouples with steel or iron as one component have complex E.M.F.-temperature relations, and that the relation between thermoelectric power and temperature is far from linear.

For some couples the thermoelectric powers of the component wires become equal and opposite in sign at some temperature known as the *neutral point*, beyond which the sign of the E.M.F. is negative. It is evidently of advantage to use couples in regions removed from their neutral point.

As shown by Stansfield, the Peltier effect $(T \frac{dE}{dt})$ is very nearly linear with the temperature for the Pt-Rh and Pt-Ir couples, but not the thermoelectric power. Sosman's observations on various Pt-Rh couples also bear out this statement.

Formulae. — Avenarius and Tait have shown that up to 300° the electromotive force of a great number of couples is represented in a manner sufficiently exact by means of a parabolic formula of two terms:

$$e = a(t - t_0) + b(t^2 - t_0^2).$$

The experiments of Le Chatelier on the platinum-palladium couple have shown that the same formula holds also for this couple up to the fusing point of palladium:

$$e = 4.3t + \frac{7.3}{1000}t^2.$$

$t = 100$	445	954	1,060	1,550
$e = 500$	2950	10,900	12,260	24,030

Platinum and Its Alloys. — This law fails completely, however, for couples made of pure platinum and an alloy of this metal. Here are three early series of determinations made with different couples, giving an idea of the order of magnitude of the E.M.F.'s of thermocouples of types used very frequently, as determined by these observers.

Barus. Pt - Pt 10% Ir.		Le Chatelier. Pt - Pt 10% Rh.		Holborn and Wien. Pt - Pt 10% Rh.	
t	e	t	e	t	e
300	2,800	100	550	100	565
500	5,250	357	2,770	200	1,260
700	7,900	445	3,630	400	3,030
900	10,050	665	6,180	600	4,920
1100	13,800	1060	10,560	800	6,970
		1550	16,100	1000	9,080
		1780	18,200	1200	11,460
				1400	13,860
				1600	16,220

Holman showed that the results of Holborn and Wien may be expressed by a logarithmic formula containing only two parameters and requiring, therefore, only two calibration temperatures. Le Chatelier showed likewise that his results could also be represented by the Holman formula, and in general it may be said that for use below 1200° C. of the thermocouple made of platinum and its alloys with rhodium and iridium, the logarithmic formula satisfies the results of observations to 2° C., or well within the limits of all except the most accurate work.

Holman's formula is as follows:

$$(1) \quad \sum_0^t e = mt^n,$$

where $\sum_0^t e$ is the electromotive force of the couple for any temperature t when the cold junction is kept at zero centigrade. The two constants are readily computed or evaluated graphically, and the resulting plot serves indefinitely for the determination of any temperature with a given couple. The equation does not apply in the region in which the thermocouple is insensitive, that is, below 250° C. It may be written, for convenience in plotting and computation:

$$(2) \quad \log \sum_0^t e = n \log t + \log m;$$

so that if $\log e$ be plotted as abscissas and $\log t$ as ordinates, a straight line is obtained.

This formula has been applied successfully to the above observations of Le Chatelier on platinum-rhodium couples and to those of Barus on platinum-iridium couples.

Holborn and Day, in their very elaborate, direct comparison of the nitrogen thermometer with thermocouples made of the various platinum metals, in the interval 300° to 1100° C., found that if a precision of 1° is sought, a three-term formula is required to express the relation between E.M.F. and temperature.

The formula

$$(3) \quad \sum_0^t e = -a + bt + ct^2$$

is the one they have used. The labor involved in computation with this form is considerable, and, unless a very great accuracy is required, Holman's formula is amply sufficient, when the uncertainty of the absolute values of high temperatures is considered.

Stansfield deduces from theoretical considerations the formula

$$(4) \quad T \frac{de}{dT} = aT + b,$$

which may be written

$$(5) \quad e = aT + b \log T + c,$$

a form which satisfies the experimental results determined with pure platinum wires. This form possesses no practical advantage over that of Holborn and Day, unless it be its usefulness, by employing the graphical method, in detecting slight errors in fusing points. The values of $\frac{de}{dT}$ at the points of fusion can be obtained from the T vs. e plot, and the T vs. $\frac{de}{dT}$ curve thus constructed throws into prominence the experimental errors at these points. As the above formulæ indicate, the curve for the platinum metals constructed with T as abscissas and $T \cdot \frac{de}{dT}$ as ordinates is a straight line. The errors of the method are less than 2° at 1000°. The ordinary metals, on the other hand, with a few exceptions such as nickel and cobalt, give nearly a straight line for the curve T vs. $\frac{de}{dT}$.

A formula which has been used on account of its more convenient form, than (3) for example, in the computation of temperature, is:

$$(6) \quad t = a + be - ce^2.$$

This formula satisfies the observations with platinum-rhodium and platinum-iridium couples in the range 300° to 1100° C. almost as well as (3).

We may compare these various formulæ by computing their deviations at various fixed points, making use of the latest data with comparison of a thermocouple (90 Pt · 10 Rh-Pt) with the gas-thermometer scale, — those of Day and Sosman, 1910. We shall assume as calibration temperatures for the three-term equations, (3), (5), and (6), the freezing points of zinc, antimony, and copper, and for Holman's equation (2), zinc and copper.

COMPARISON OF THERMOELECTRIC FORMULÆ
(Pt — 90 Pt · 10 Rh)

Substance.	Freezing point.	Observed (microvolts).	Observed — calculated temperatures.			
			(2)*	(3)	(5)	(6)
Cadmium	320.0°	2,502	-0.2	-0.3	+ 6.9	- 1.1
Zinc	418.2	3,429	0	0	0	0
Antimony	629.2	5,529	+2.3	0	0	- 0.1
Silver	960.0	9,111	+2.5	+ 0.2	+ 2.2	- 0.9
Gold	1062.4	10,296	+0.4	+ 0.2	0	0
Copper	1082.6	10,535	0	0	0	+ 0.1
Diopside	1391	14,231	-6	+10	-10	+19
Nickel	1452	14,969	-6	+14	-11	+28
Cobalt	1490	15,423	-7	+14	-13	+31
Palladium	1549	16,140	-5	+20	-14	+42
Platinum	1755	18,613	+1	+42	-15	+73

* The numbers in parentheses refer to formulæ on preceding pages.

It is evident from the table that we have, therefore, as many thermoelectric scales as we have equations. The two formulæ which best fit the region 300° to 1100° C., namely, (3) and (6), are clearly not suited for extrapolation without applying proper corrections. Of all the formulæ, Holman's (2), which is also the simplest, is the best suited for general use throughout the whole range 300° to 1750°, giving a maximum error of 2.5° below, and of 7° above, 1100° C. None of these equations is satisfactory for the most exact work, however. A cubic equation in t will satisfy the data more exactly, but this is extremely inconvenient to solve for t ; or two parabolas of type (3) may be used, the first from 300° to 1100°, the second from 1100° to 1750°.

In 1905, Harker, using thermocouples of platinum against a 10 per cent rhodium and 10 per cent iridium alloy of platinum, respectively, and extrapolating equation (3) from 1100° C.,

obtained 1710° C. with both types of thermocouple as the uncorrected value of the platinum melting point. This value, 1710° C., has been generally accepted in many quarters as the true melting point of this metal. Waidner and Burgess, however, demonstrated in 1907 that the value found for high melting points by extrapolating with thermocouples depends not only on the thermoelectric relation assumed, but also on the nature of the couple. Some of their results for the palladium and platinum melting points are given below, the calibration equations and temperatures being the same as in the above.

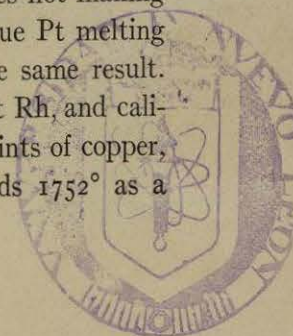
EXTRAPOLATION WITH VARIOUS THERMOCOUPLES.

Type of couple.	Equation.	Palladium, MP = 1549.	Platinum, MP = 1755.
4 of Pt, 90 Pt — 10 Rh (approx.)	{ (3)	1521° to 1537°	1698° to 1715°
2 makers.....	(2)	1536 to 1561	1717 to 1754
2 of Pt, 90 Pt — 10 Ir	{ (3)	1525 to 1528	1705 to 1710
2 makers.....	(2)	1516 to 1541	1697 to 1728
2 of 90 Pt — 10 Rh, 80 Pt — 20 Rh	{ (3)	1507	1687 to 1710
	(2)	1531	1734 to 1755
2 of Ir, 90 Ir — 10 Ru.....	{ (3)	1533 to 1551	1704 to 1738
	(2)	1517 to 1565	1676 to 1757

It would appear from these data that the corrections to apply to a given type of thermocouple computed and extrapolated with a given formula are uncertain, the slight variations in composition of the alloy wire from one couple to another apparently producing considerable differences in the computed temperatures.

It is an interesting fact that the 10 per cent alloys of Rh and Ir with Pt, when treated by equation (3), give very exactly the same temperature scale to the melting point of platinum, although the actual shapes of the E.M.F. temperature curves are very different for those two couples, that for Pt — Ir being the more nearly linear. It was an instructive case of two negatives not making an affirmative to assign the value 1710° as the true Pt melting point because both Ir and Rh couples led to the same result.

Using Pt-Rh couples of 1, 5, 10, and 15 per cent Rh, and calibrating in terms of equation (3) at the melting points of copper, diopside, and palladium (see above), Sosman finds 1752° as a mean value for Pt with a range of only 7°.



Variation of E.M.F. with Composition. — Sosman has also studied this for the Pt-Rh couples, and some of his results are given in Fig. 24. It will be noticed that in the region of the 10 per cent alloy, which is the one most commonly met with, or at least such is the nominal composition usually given, a change of 1 per cent in composition is equivalent to about 50° at 1000° .

The Base-metal Couples. — The E.M.F.-temperature relation for some of these couples, of which there are a great many in use, is very nearly linear. For some couples, on the other hand, the E.M.F.-temperature relation is very complex; and in those cases in which there are allotropic or other transformations within the material, taking place over a temperature range or along the wire as the successive portions are heated or cooled, there sometimes occur inflections in the curve, producing regions of considerable extent in which the couple is relatively very insensitive. When such inflections occur, there is usually no conveniently expressed relation between E.M.F. and temperature (see Fig. 23). We shall call attention later to some specific cases of base-metal thermoelectric formulæ.

Methods of Measurement of Temperature. — Two methods may be used to measure the electromotive force of a couple: the method of opposition and the galvanometric method. From the scientific point of view, the first alone is rigorous; it is usually made use of in laboratories. The second method is simpler, but possesses the inconvenience of giving only indirectly the measure of the electromotive force by means of a measurement of current strength. This inconvenience is more apparent than real in the later forms of instrument, as will be shown.

There are sources of error, however, inherent in the galvanometric method, such as effects of lead resistance and temperature coefficients of leads and galvanometer, which, as we shall see, are difficult if not impossible of complete elimination even with the best apparatus available. The method of opposition, on the other hand, may be made, in so far as the measurements of E.M.F. are concerned, as exact as may be desired, or so that

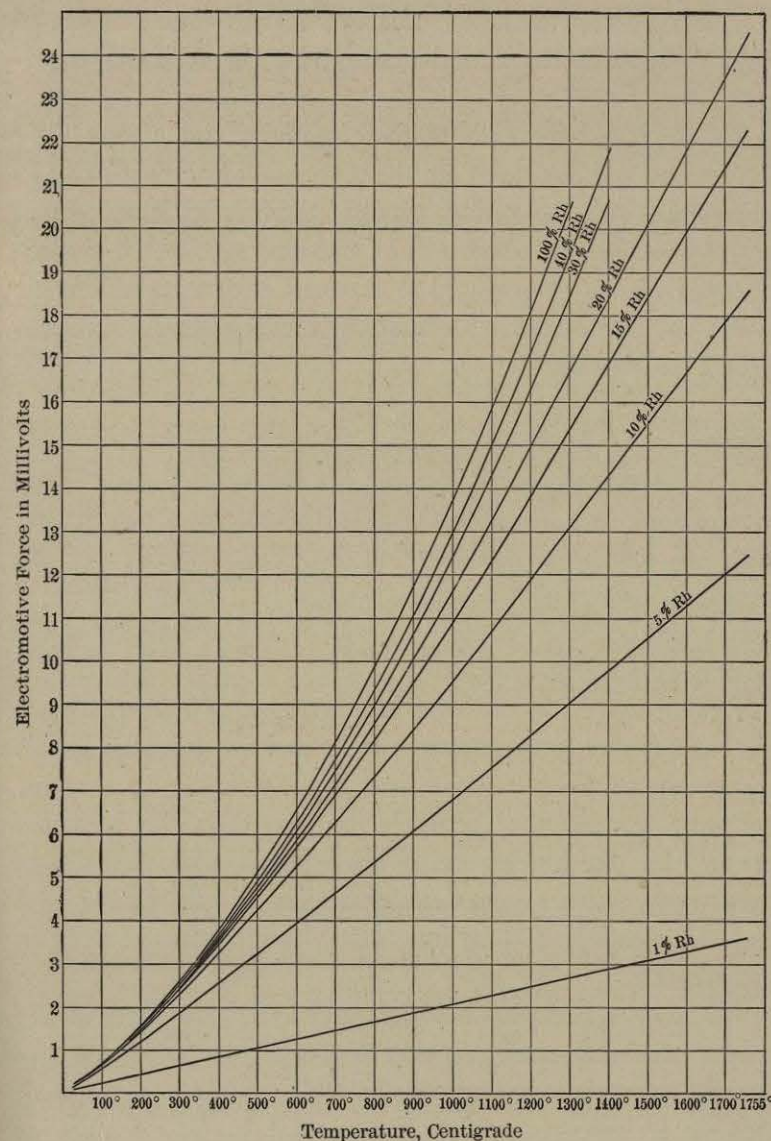


Fig. 24. E.M.F. of Pt-Rh Thermocouples.

the only outstanding uncertainties are inherent in the thermocouple itself. These uncertainties, such as inhomogeneity and conduction along the wires, variable zero, and actual change of E.M.F., are sometimes overlooked, giving rise to illusory accuracy.

We shall describe each of these methods and discuss their limitations, and also point out the sources of error most likely to be present with the various types of thermoelectric apparatus.

Galvanometric Method.—The measurement of an electromotive force may be reduced to that of a current; it suffices for that to put the couple in a circuit of known resistance, and from Ohm's law we have

$$E = \frac{I}{R}.$$

If the resistance is not known, but is constant, the electromotive force will be proportional to the current strength, and that will suffice, on the condition that the calibration of the couple is made with the same resistance. If this resistance is only approximately constant, the relation of proportionality will be only approximately exact.

This method is the one used in practically all industrial practice, and to-day galvanometers can be had satisfying all the requirements of which we shall treat in the following paragraphs. In many quarters the thermoelectric pyrometer has been discredited because instruments giving evidently unreliable results were used. With a better understanding of the requirements and the meeting of them by manufacturers, this prejudice is disappearing.

Resistance of Couples and Galvanometer.—The wires of the couple make necessarily a part of the circuit in which the current strength is measured, and their resistance varies with increase of temperature. It is important to take account of the order of magnitude of this inevitable change of resistance.

Barus made a systematic series of observations on the alloys of platinum with 10 per cent of other metal. The relation

between the resistance and the temperature being of the form

$$R_t = R_0(1 + \alpha t),$$

he obtained the following results:

	Pt (pure)	Au	Ag	Pd	Ir	Cu	Ni	Fe	Cr	Sn
Specific resistance in microhms (R)	15.3	25.6	34.8	23.9	24.4	63.9	33.7	64.6	42	39
1000 α	2.2	1	0.7	1.2	1.2	0.2	0.9	0.4	0.5	0.7

Other tests gave the figures below:

	5% Al	5% Mn	10% Mo	5% Pb	2% Sb	5% Bi	2% Zn	5% Zn
R_0	22	50	17.6	7.7	29.5	16.6	47.8	25
1000 α	1.5	0.4	1.9	1.8	1	2	0.3	1.1

The coefficient α is taken between 0° and 357° (boiling point of mercury).

The experiments of Le Chatelier, for the couples that he used, gave the following results:

For platinum,

$$R = 11.2(1 + 0.002 t) \text{ between } 0^\circ \text{ and } 1000^\circ.$$

For platinum-rhodium (10% Rh),

$$R = 27(1 + 0.0013 t) \text{ between } 0^\circ \text{ and } 1000^\circ.$$

Holborn and Wien found for pure platinum,

$$R = 7.9(1 + 0.0031 t) \text{ between } 0^\circ \text{ and } 100^\circ,$$

$$R = 7.9(1 + 0.0028 t) \text{ between } 0^\circ \text{ and } 1000^\circ.$$

Very commonly couples are made of the platinum metals of wires 1 m. in length and 0.5 mm. in diameter; their resistance, which is about 2 ohms cold, is doubled at 1000° . If use is made then of a galvanometer of a resistance of 200 ohms, and if the variation of the resistance of the couple is neglected, the error is equal to $\frac{1}{100}$. In general this error is still less except in certain

industrial uses. Thus in the laboratory the length heated is often less than 10 cm., and then the error reduces to $\frac{1}{1000}$.

We may calculate the effect of resistance in the electrical circuit, including that of the couple and galvanometer, on the reading of the pyrometer galvanometer in the following way: If E is the true E.M.F. generated by the thermocouple and E' the E.M.F. indicated by a galvanometer of resistance R , in series with the couple and leads, of resistance r and r' respectively, then

$$E = \frac{E'(R + r + r')}{R}.$$

In the case of certain industrial installations, where the galvanometer is at a distance from the couple, the value of r' , the resistance of the copper wires connecting the couple to the galvanometer, may be of as great importance as that of the couple wires, r . The value of r' can of course be kept down, however, by increasing the size of wire used.

Although in the case of platinum couples, which on account of cost, high specific resistance, and temperature coefficient of the materials necessarily have an appreciable resistance and therefore require a relatively high resistance galvanometer, it should be noted that, with base-metal couples of large cross section and consequently low resistance, galvanometers of very much lower resistance, and therefore of a more robust type, in general, may be allowed here. For example, if the couple has a resistance of 0.1 ohm and the connecting leads a negligible resistance, as may readily happen with certain types of pyrometer rod, the galvanometer may be a millivoltmeter of only 10 ohms without introducing errors over $\frac{1}{100}$, or 10% at 1000° C., due to this cause.

Pyrometer Galvanometers.—It may still be of interest to recall the historical development of this phase of the subject, as it offers a good illustration of the influence of one field of activity on another, and from the fact that the difficulties encountered and the precautions to be taken in the construction and use of these instruments are not yet sufficiently well appreciated by

some manufacturers as well as by many experimenters and other users.

The earliest measurements, those of Becquerel and of Pouillet, were made with needle galvanometers controlled by terrestrial magnetism. Such apparatus, sensible to jarring, requires delicate adjustment, and the readings take a long time. The use of these instruments would have prevented the method from becoming practical. It is only thanks to the use of movable-coil galvanometers of the Deprez-d'Arsonval type that the thermoelectric pyrometer has been able to become, as it is to-day, an apparatus in current usage.

This apparatus, in one of its earlier forms (Fig. 25), is composed of a large horseshoe magnet between whose poles is suspended a movable frame through which the current passes. The metallic wires, which serve at the same time to suspend the coil and bring in the current, undergo then a torsion which is opposed to the displacement of the coil.

The latter stops in a position of equilibrium which depends both on the strength of the current and the value of the torsion couple of the wires. To these two forces is added, in general, a third, due to the weight of the coil, which causes disturbing effects often very troublesome. We shall speak of this further on.

The measurement of the angular displacement of the coil is made sometimes by means of a pointer which swings over a divided scale, more often by means of a mirror which reflects on a semitransparent scale the image of a wire stretched before a small opening conveniently lighted.

These movable-coil galvanometers were for a long time considered by physicists as unsuited for any quantitative measurements; they were only employed in null methods and made accordingly. In order to render them suitable for quantitative

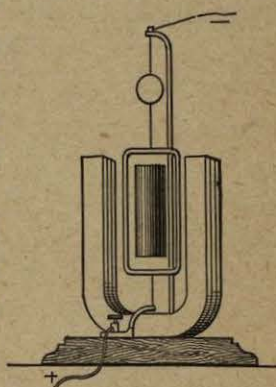


Fig. 25. Moving-coil Galvanometer.