DELTA CONTROLS CORPORATION

SHREVEPORT ENGINEERING DEPARTMENT DOCUMENT

THERMOCOUPLE PROPERTIES AND CONSIDERATIONS WHEN BEING USED IN VERY HIGH TEMPERATURE CLAUS REACTORS, GASSIFIERS AND POX UNITS

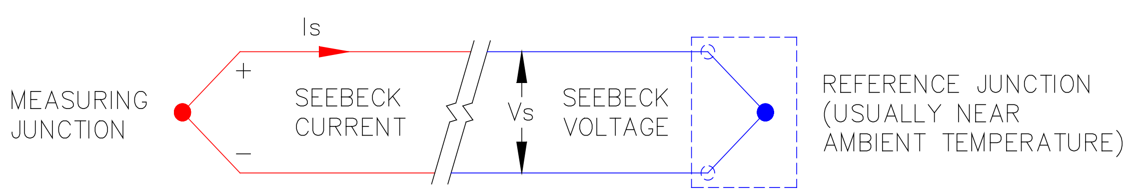
Thermocouples are inherently accurate, primary temperature measuring devices. Their accuracy is traceable to the NIST (National Institute of Standards and Technology). They are highly reliable, easy to understand and have been commonly used for over a hundred years.

T. J. Seebeck, 1821, while observing electromagnetic effects in copper and antimony alloy metals, discovered that an electric current (Seebeck current) flows continuously in a closed loop of two dissimilar metals when the two metal junction points are maintained at different temperatures. With the loop opened at the reference end, a voltage (Seebeck voltage) develops proportional to the temperature difference and the composition of the two metals (usually alloys).

A thermocouple consists of two dissimilar metal wires joined to each other at both ends. The temperature of one joined end is used as a reference (sometimes called the “cold junction”). It is either held at a constant temperature or its temperature is accurately measured. The other joined end is the measuring end (sometimes called the “hot junction”).

When the loop is opened and the two junction ends are at different temperatures, a small voltage difference between the two ends is developed. This voltage is proportional to the temperature difference between the two ends. Thus, knowing the temperature of the reference end and adding the temperature represented by the differential voltage, the actual absolute temperature of the measuring end is accurately known. The measurement can be done to extremely high accuracies by certification of the thermocouple being used. This is done at a precision temperature laboratory by subjecting the thermocouple to be certified to various “standard temperatures”. An actual output millivoltage to temperature measured chart is made. This is compared with the theoretical “standard” ANSI millivoltage to temperature chart. A “correction chart” for the subject thermocouple can now be used to measure unknown temperatures traceable to an NIST standard of accuracy.

BASIC THERMOCOUPLE CIRCUIT

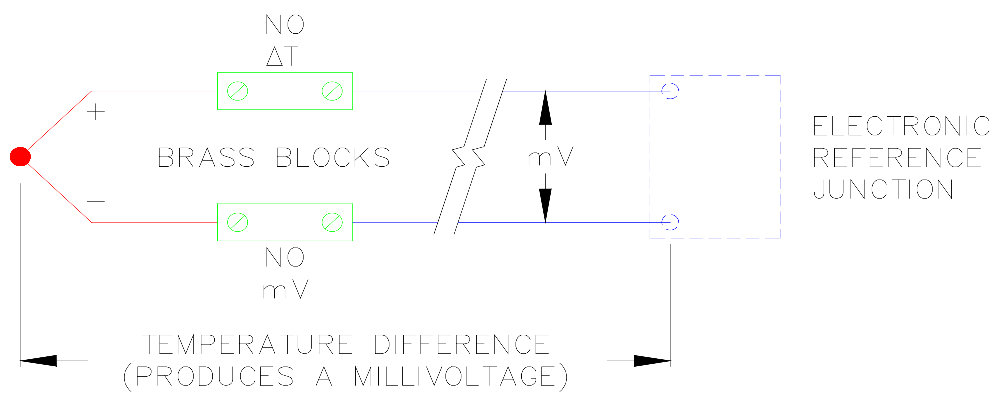


The reference junction is commonly replaced by an electronic device (shown dotted above). It produces the same millivoltage that an actual thermocouple junction would, referenced at a selected temperature (typically zero degrees). This eliminates the need to measure and add or subtract the current reference junction temperature to be able to read the correct temperature of the hot junction. The net millivoltage produced is a function of the composition of the two metals and the temperature difference between the junctions. Adding the selected (or measured) reference temperature to the temperature equivalent of the differential millivoltage results in the true absolute temperature of the measuring junction. This is inherent and intrinsic to a thermocouple and is not dependent on an adjustable calibration done by an instrument technician or operator.

LOCATION OF THE REFERENCE JUNCTION

It is common to locate the reference junction a considerable distance away from the measuring junction. This is done for reasons of personnel safety and convenience, such as where the ambient temperature is too high for an electronic transmitter or a maintenance technician to survive. This is done by adding an additional length of wire to both the positive and negative thermocouple legs. It "extends" the reference junction to a more suitable place without affecting accuracy. This wire is called "leadwire" and is of the same material as the thermocouple, or of an alloy that has the same millivolts output per temperature unit as the thermocouple. Leadwire is not normally conforming or tested above 400°F (200°C), and its output millivoltage may deviate somewhat from the thermocouple at higher temperatures, causing measurement errors.

The Seebeck effect is zero if there is no temperature differential between the two junctions. Short heavy brass or silver connecting terminals (good heat conductors) are normally used to attach the leadwire to the thermocouple wire. Both terminal screws and wires are heat sinked to the metal block so that all are at the same temperature. The terminal connection, even though of a different material than the thermocouple, does not effect the reading or accuracy of the thermocouple output signal because there is no temperature difference across the connection.



SELECTING THERMOCOUPLE METALS AND "TYPES"

The measurement millivoltage generated by the selected dissimilar metals should be fairly linear over the temperature range of interest for ease of usage. The two dissimilar thermocouple metals should be readily available in certain exact "standard" compositions. This allows a "standard chart"; of temperature versus millivoltage readings, to be produced. This is done by varying the temperatures and recording the millivoltage over a large number of points, under laboratory conditions. This only need be done one time to produce a "standard" chart for a particular metallic composition. Thereafter, the temperature may be read from the "standard chart" according to the millivoltage produced by those two "standard type" metallic compositions. This can be done for any two dissimilar metals and the output millivoltage will be the same for any additional units built. Each wire is commonly called a "leg", one positive and one negative.

Scientist and engineers have selected several metallic compositions as "standards" because they meet the range and linearity needs of most users. Just as importantly, they are inherently calibrated when built and need not be individually calibrated before use. Each pair of standard compositions is designated as a "Type" which is followed by an alphabetical letter; eg. "Type B". Each wire of the Type "B" thermocouple is composed of exact percentages of platinum and rhodium metal.

GENERALLY ACCEPTED THERMOCOUPLE "TYPES"

ANSI LETTER DESIGN	LEG∈	METALLIC COMPOSITION	MELTING POINT		USABLE PRACTICAL TEMPERATURE RANGE	TOLERANCES (THE GREATER OF BASE OR % OF READING)	
			°F	°C		** STANDARD	PREMIUM
B	P N	PLATINUM - 30% RHODIUM PLATIMUM - 6% RHODIUM	3320	1825	400 TO 3050 °F 200 TO 1680 °C	±0.5%	NOT ESTABLISHED
C *	P N	(TUNGSTEN - 5% RHENIUM) (TUNGSTEN - 26% RHENIUM)	4500	2480	30 TO 4200 °F 0 TO 2300 °C	NOT ESTABLISHED SEE IPTS –90	N.A.
E	P N	CHROMEL®, CONSTANTAN	2230	1220	-300 TO 850°F -200 TO -450°C	± 1.7°C OR ±0.5%	±1.0 °C OR ±0.4%
J	P N	IRON CONSTANTAN	2230	1220	30 TO 700° F 0 TO 400°C	±2.2°C OR ±0.75%	±1.1 °C OR ±0.4%
K	P N	CHROMEL®, ALUMEL®,	2550	1400	-300 TO 1800° F -200 TO 1000°C	±2.2° C OR ±0.75%	±1.1°C OR ±0.4%
N	P N	NICROSIL ® NISIL®	2440	1340	30 TO 1800°F 0 TO 1000°C	±2.2° C OR ±0.75%	±1.1°C OR ±0.4%
R	P N	PLATINUM - 13% RHODIUM PURE PLATINUM	3215	1770	32 TO 2700°F 0 TO 1500°C	±1.5°C OR ±0.25%	±0.6°C OR ±0.1%
S	P N	PLATINUM - 10% RHODIUM PURE PLATINUM	3215	1770	32 TO 2700°F 0 TO 1500°C	±1.5°C OR ±0.25%	±0.6°C OR ±0.1%
T	P N	COPPER CONSTANTAN,	1980	1080	-450 TO 400°F -270 TO 200°C	±1.0°OR ±0.75%	±0.5°C OR ±0.4%

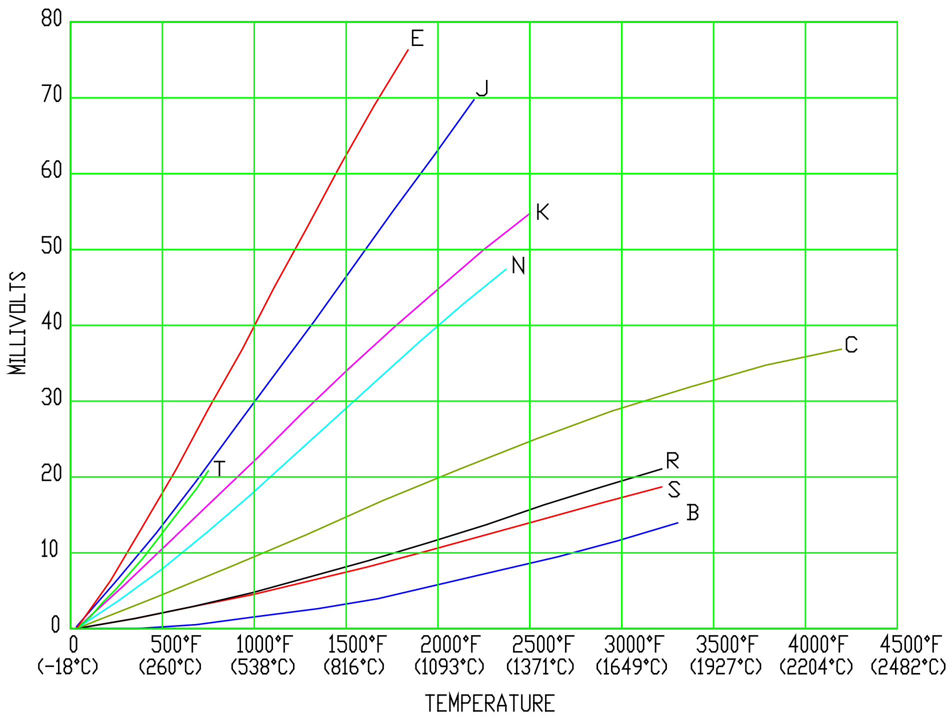
* Not an ANSI symbol, but is commonly used as a designated name; also sometimes referred to as a Type "W".
® Trademark of Hoskins Mfg
∈ P=Positive LegN = Negative Leg

**"Standard" grade wire is sufficiently accurate for most applications. The purity and composition of "premium" grade wire is more closely controlled, and its millivoltage output is closer to the NIST standard chart and therefore reads somewhat more accurately than the "standard" grade does.

NOTE: Individual T/C units may be calibrated by measuring their output at several known temperatures and preparing an error correction chart. This chart is used to eliminate any deviation from the "standard" output millivoltage versus temperature readings inherent in this particular thermocouple. The result is known as an "NIST" traceable thermocouple.

MAXIMUM RANGES OF STANDARDIZED THERMOCOUPLE TYPES

(EACH WIRE IS MADE OF A PARTICULAR ELEMENT OR METALLIC ALLOY)
*See table above for usable ranges in industrial processes



INTERNATIONAL DESIGNATION STANDARDS

Most industrialized countries accept the same composition standards and "Type" numbers listed above. Color coding designations vary, depending on the national standard. Jacket colors are used to differentiate between thermocouple types.

COUNTRY	T/C STANDARD
USA	ANSI MC96-1-82
GERMANY	DIN 43710
JAPAN	JIS C1602
UNITED KINGDOM	BS4937
FRANCE	NF C42-321
ITALY	CTI-UNI 7938
IEC	584-1: 1977

T/C TYPE	ANSI MC96-1-82		UK BS 1843	GERMANY DIN 43714	JAPAN JIS C1610-1981	FRANCE NF C42-323
	THERMOCOUPLE WIRE	EXTENSION LEADWIRE				
B (OVERALL) BP BN	* - -	GREY +GREY -RED	- - -	GREY +RED -GREY	GREY +RED -WHITE	- - -
E (OVERALL) EP EN	BROWN +PURPLE RED	PURPLE +PURPLE -RED	BROWN +BROWN -BLUE	BLACK +RED -BLACK	PURPLE +RED -WHITE	- - -
J(OVERALL) JP JN	BROWN +WHITE -RED	BLACK +WHITE -RED	BLACK +YELLOW -BLUE	BLUE +RED -BLUE	YELLOW +RED -WHITE	BLACK +YELLOW -BLACK
K(OVERALL) KP KN	BROWN +YELLOW -RED	YELLOW +YELLOW -RED	RED +BROWN -BLUE	GREEN +RED -GREEN	BLUE +RED -WHITE	YELLOW +YELLOW -PURPLE
N(OVERALL) NP NN	BROWN +ORANGE -RED	ORANGE +ORANGE -RED	- - -	- - -	- - -	- - -
R(OVERALL) RP RN	* * *	GREEN +BLACK -RED	GREEN +WHITE -BLUE	- - -	BLACK +RED -WHITE	- - -
S(OVERALL) SP SN	* * *	GREEN +BLACK -RED	GREEN +WHITE -BLUE	WHITE +RED -WHITE	BLACK +RED -WHITE	GREEN +YELLOW -GREEN
T(OVERALL) TP TN	BROWN +BLUE -RED	BLUE +BLUE -RED	BLUE +WHITE -BLUE	BROWN +RED -BROWN	BROWN +RED -WHITE	BLUE +YELLOW -BLUE

* None set, but brown is used by convention for woven high temperature jackets; black for positive wire jackets and red for negative jackets.

** Extension leadwire is stranded and made of materials with characteristics similar to the thermocouple wires. For a type "J", it is made of a copper-nickel alloy to improve corrosion resistance. For Types "R" & "S", leadwire is made of a copper alloy. In this case the intent is to lower the cost of the leadwire. For Type "B", the leadwire is made of pure copper (up to 200 °F (100°C) ambient temperature, again to lower the cost.

USEFULNESS OF BASE METAL TYPE THERMOCOUPLES

The Type "K" thermocouple is a base metal Type which can reliably measure temperatures continuously, with proper protection, up to 1800°F (1000°C) it can, theoretically, measure to 2400°F for a short period of time. It is recommended for and does a good job during refractory liner dryout and while bringing the furnace up to 1800°F (1000°C). It is useful only during the initial startup of a Claus, POX, or incinerator unit. It deteriorates rapidly and must be considered to be sacrificial after refractory dryout and the initial curing phase is completed. It fails because:

(a) Sulphurous gases rapidly attack the wires above 800°F (475°C) through the mechanism of intergranular corrosion.
(b) Failure mode is a falling of output signal, (reads low) as it corrodes. Embrittlement and breakage due to vibration soon causes complete failure.
(c) Preferential loss of chromium, over time, at elevated temperatures, also causes a downwards calibration drift.

The Type "N" thermocouple is very similar to the Type "K". It was developed as an improvement over the Type "K". Its primary advantage is better stability in nuclear applications. It is no more suitable than the Type "K" for very high temperature reactor service.

Types "E", "J", and "T" are the other common base metal thermocouples. They are used for low and moderate temperature services. None is suitable for continuous service above 1000°F (540°C) and therefore not suitable for very high temperature reactors and incinerators.

Type "C" thermocouple will measure to over 4000°F (2200°C); however it is primarily limited to laboratory and research applications. It is not practical for and will not withstand the rigors of typical high temperature process environments. The main reasons are:

(a) It must be operated in a vacuum or under an inert gas. Hot tungsten burns when exposed to oxygen. This type failure happens when a glass light bulb breaks.
(b) Tungsten becomes embrittled as it is heated and cooled over a range of temperatures. Normal vibration in an incinerator or Claus unit causes failure due to breakage of the embrittled wire, even in an inert gas atmosphere. Type "C" can be used in certain applications, but is not suitable for most industrial process services. A type "C" thermocouple or a radiation pyrometer should be considered when the service temperature is above 3100°F (1700°C).

SELECTING A THERMOCOUPLE FOR HIGH TEMPERATURE REACTORS

The Delta model HTP is used for high temperature difficult services. These services include Claus thermal reactors, gassifiers, POX converters, chemical incinerators, etc. Acid or caustic environments, at temperatures from 1800° to 3100° F (1000 to 1700°C), will degrade many ceramics and almost all metals. Such high temperatures and gas conditions also limit the types of thermocouples that can be used. The noble metal types, "B", "R", and "S" have been found to be accurate, reliable, long lived, and generally satisfactory. The caveat is that they must be protected from elemental hydrogen, sulphurous compounds, and several trace elements.

The Type "R" is the best choice when the normal temperature does not exceed 2700°F (1500°C). It will withstand up to 2900 °F (1600°C), maximum, for occasional short-term excursions. One wire is pure platinum and the other is an alloy of platinum and 13% rhodium. It has a relatively high millivolt output signal versus temperature. It is insensitive to common vibration levels and rapid temperature changes.

The Type "S" is the same as the Type "R" except that it only contains 10% rhodium. It also produces a lower differential millivolt output signal than the Type "R" does. The Type "S" is an older standard and rarely used today.

The Type "B" thermocouple is suitable for temperatures up to 3000°F (1650°C) continuous with short-term excursions to 3150°F (1730°C). One wire is an alloy of platinum with 6% rhodium. The other wire is an alloy of platinum with 30% rhodium. It has a relatively low millivoltage output signal. It is somewhat more sensitive to contamination by some gases than is the type "R". However, with proper protection, the type "B" will perform reliably in the most difficult applications, and do so at higher temperatures. The type "B" operates at the highest temperature of any commonly used rugged industrial process thermocouple.

PROTECTION OF NOBLE METAL THERMOCOUPLES

Platinum-rhodium thermocouples are the only Types that have been successfully used at very high temperatures in Claus sulphur plant reactors, POX units and industrial chemical destruction incinerators. They have the potential to provide highly accurate and reliable measurements, over long periods of time, in these difficult applications. However, elemental hydrogen, sulphur, and some other atomic contaminents must be excluded from contacting them. If these contaminents are not totally excluded, then significant calibration drift, embrittlement and failure of the thermocouple wire will occur. In addition, certain elements act as catalyzers and must also be excluded from the vicinity of the thermocouple wires.

Delta Controls has developed a pressurized flush system that accomplishes these objectives. This system is part of a thermocouple unit known as the “HTP”. It has been proven in hundreds of installations, worldwide, for more than 25 years. It can provide years of reliable service when installed in accordance with the instructions. For more information, see detailed discussions of this sensor at the Delta Controls technical website.

Attempts have been made to protect the thermocouple wires by using other, seemingly “simple” methods. None has been successful in Claus reactors, POX units, or chemical incinerators. One of these “simple” designs was originally developed for measuring gas temperatures in military gas turbines. Basically it uses an “absorber” to shield the thermocouple from hydrogen. The “absorber” has limited capacity and is quickly overcome by the copious amounts of hydrogen to be absorbed in a Claus thermal reactor application. A downwards calibration drift then begins, accuracy is poor, and complete failure occurs soon thereafter.

A similar thermocouple design utilizes a barrier around the element wires that preferentially allows hydrogen to penetrate to the inside and fill the space around the wires. The idea is to exclude oxygen, which corrodes this type thermocouple. This design has been used, with some success, for temporary measurements. The hydrogen causes the embrittlement problem to worsen and failure due to breakage soon occurs. It has not been successful for long service in a Claus thermal reactor.

Designs adopted from thermocouples used in the metals industry have also been tried in difficult reactor service. Some designs had vent holes so that the permeating gases could escape. Some used the opposite approach and were pressurized to keep them out. Some used a continuous purge of the well to quickly remove them. These designs did not solve the accuracy and failure problems and in some cases, created new problems.

The Model HTP is the only thermocouple based temperature sensor designed specifically for use in Claus thermal reactors. The HTP, properly installed and operated, works reliably in this service and has over 25 years of worldwide service history, in hundreds of plants, to prove it.

This document is intended to provide general information only. For specific recommendations and limitations, please provide Delta Controls with details of your process and application.

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