

CRYOGENICS PRIMER

TEMPERATURE

According to Webster's Dictionary, temperature is "the degree of hotness or coldness of anything, usually as measured on a thermometer." The question is, what scale does that thermometer use?

In the early years of cryogenic research, the establishment of an accurate, reliable and reproducible temperature scale was no easy matter (Scurlock 484). Early scales were assigned arbitrary numerical values to represent coordinate states of temperature values. Laboratories developed their own scales according to the fixed point of various materials. The fixed point they used depended on the substance they were studying.

What's a fixed point? A fixed point is a specific temperature for a specific material based on the material's triple point. The standard fixed point used in modern thermodynamics is the triple point of water, which is 273.16 °K.

What's a triple point? First let's describe phase equilibrium: phase equilibrium is the one temperature where a material coexists in either its solid and liquid form (melting point) or its liquid and vapor form (boiling point) with no phase exchange. Therefore, the triple point is where the solid, liquid, and vapor coexist in equilibrium. There is only one temperature and pressure where the triple point of a particular substance is possible.

Anders **Celsius** (1701-1744), a Swedish astronomer and inventor, designed a thermometer scale that made the freezing point of water 0°, and the boiling point 100°C.

<u>Celsius</u>	
-273.16°C	Absolute zero
0°C	Triple point of water
100°C	Boiling point of water

Gabriel **Fahrenheit** (1686-1736), a German physicist who designated the scale which uses 32°F as the freezing point of water and 212°F as the boiling point.

<u>Fahrenheit</u>	
-459.67°F	Absolute zero
32°F	Triple point of water
212°F	Boiling point of water

William John MacQuorn **Rankine** (1820-1872), a Scottish physicist who designated an absolute temperature scale where the measurement interval equals a Fahrenheit degree, but his 0° point is equal to -459.67°F. According to this scale, the freezing point of water is 491.67°R.

Rankine

0°R	Absolute zero
491.68°R	Triple point of water
672°R	Boiling point of water

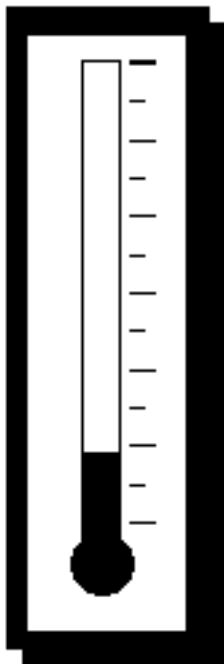
William Thomson **Kelvin** (1824-1907), a British physicist and mathematician who designated a scale of thermodynamic temperature that uses absolute zero as its beginning point, but is not referenced to a substance. Room temperature is ~ 300°K.

Kelvin

0°K	Absolute zero
273.16°K	Triple point of water
373.14°K	Boiling point of water

TEMPERATURE SCALE

In thermodynamic terms, the more interesting range of temperature for cryogenics is that from zero to 100° Kelvin. As you will see in future chapters, there is a direct relationship between absolute zero and entropy. (Entropy must be reduced to produce low temperatures.) The third law of thermodynamics says that absolute zero can't be reached. It's obvious, then, that the closer we come to absolute zero "the more difficult it is to obtain a unit temperature decrease"(Van Sciver 2). A linear scale won't represent this fundamental fact, a logarithmic scale would be more meaningful.

CONVERSION FACTORS

$$^{\circ}\text{K} = ^{\circ}\text{C} + 273.15$$

$$^{\circ}\text{K} = (5/9) (^{\circ}\text{F} + 459.67)$$

$$^{\circ}\text{K} = (5/9) ^{\circ}\text{R}$$

$$^{\circ}\text{C} = (5/9) (^{\circ}\text{F} - 32)$$

$$^{\circ}\text{C} = ^{\circ}\text{K} - 273.15$$

Example

$$^{\circ}\text{C} = (5/9) (^{\circ}\text{F} - 32)$$

$$^{\circ}\text{C} = (5/9) (70^{\circ}\text{F} - 32)$$

$$^{\circ}\text{C} = 5/9 * 38$$

$$^{\circ}\text{C} = 21.11$$

$$^{\circ}\text{K} = ^{\circ}\text{C} + 273.15$$

$$^{\circ}\text{K} = 21.11 + 273.15$$

$$^{\circ}\text{K} = 294.26$$

ABSOLUTE ZERO

Absolute zero **cannot** be reached — that is the third law of thermodynamics. Both Nernst and Einstein confirmed this theory originally stated by the Carnot principle. Further, according to Sears, it would be wrong to say that all molecular activity stops at absolute zero, "Rather, at absolute zero the system has its minimum possible total energy (kinetic plus potential), although this minimum amount is in general not zero"(Sears 347). A further explanation of the three law of thermodynamics, the Carnot principle, and absolute zero can be found in the section on **Thermodynamic Laws**.

TYPICAL CRYOGENIC FLUIDS

CHANGES OF STATE

When a substance changes state, its molecules do not change, only their relation to each other. **Solid-state** molecules are free to move, but are kept in a rigid pattern by "tethers" of mutual attraction which cause them to form crystals. The molecules of **Melting** and **subliming** substances both need an extra dose of energy (**latent heat**) to break their attraction tethers. Liquid surface tension is a barrier caused by the unequal pull on molecules at the surface by the molecules inside the liquid. The **evaporation** and **condensation** of individual molecules go on at the same time, but the net effect is usually one or the other — evaporation or condensation. With **saturation** in a closed vessel, molecules reentering the liquid equal those leaving the liquid as long as temperature is kept constant. Boiling (bubbles forming) in an open vessel takes place when the vapor pressure is equal to or greater than the external pressure.

GAS LAWS

Except near their condensing points, most gases follow these rules:

1. For a given pressure, gas expands in exact proportion to absolute temperature.
2. For a given volume, the absolute pressure of a gas varies in exact proportion to the absolute temperature.
3. For a given temperature, the volume of a given weight of gas varies inversely to the absolute pressure.

These three rules can be summed up in one formula: $P \times V = k \times T$.

P = absolute pressure (lb. per sq. in.)

V = specific volume (cu. ft. per lb.)

T = absolute temperature (degree. F plus 460)

k = 10.7 divided by molecular weight of gas (k for air equals 0.37)

NITROGEN

Liquid nitrogen is inert, colorless, odorless, noncorrosive, extremely cold, and nonflammable. The molecular symbol for nitrogen is N₂. Liquid nitrogen has an expansion ratio of 1 to 694. It can produce suffocation by diluting the concentration of oxygen in the air below levels necessary to support life.

Boiling Point @ 1 atm	77.32°K	-320.5°F	-195.8°C
Freezing Point @ 1 atm	83.4°K	-346.0°F	-210.0°C
Critical Temperature	126.1°K	-232.4°F	-146.9°C
Critical Pressure	493 psia (33.5 atm)		

ARGON

Liquid argon is inert, colorless, odorless, noncorrosive, extremely cold, and nonflammable. The molecular symbol for argon is Ar. Liquid argon has an expansion ratio of 1 to 840. It can produce suffocation by diluting the concentration of oxygen in the air below levels necessary to support life.

Boiling Point @ 1 atm	87.4°K	-297.6°F	-185.9°C
Freezing Point @ 1 atm	63.46°K	-308.9°F	-189.4°C
Critical Temperature	150.8°K	-188.4°F	-122.4°C
Critical Pressure	705 psia (48.0 atm)		

HELIUM

Liquid helium is inert, colorless, odorless, noncorrosive, extremely cold, and nonflammable. The molecular symbol for helium is He. Liquid helium has an expansion ratio of 1 to 700. It can produce suffocation by diluting the concentration of oxygen in the air below levels necessary to support life.

Boiling Point @ 1 atm	4.26°K	-452.1°F	-268.9°C
Freezing Point @ 1 atm	-----	-458.0°F	-272.2°C
Critical Temperature	5.2°K	-450.3°F	-268.0°C
Critical Pressure	33.2 psia (2.26 atm)		

HYDROGEN

Liquid hydrogen is highly flammable, colorless, odorless, noncorrosive, and extremely cold. The molecular symbol for hydrogen is H₂. It can produce suffocation by diluting the concentration of oxygen in the air below levels necessary to support life. Its explosive limits, when mixed with air, are 4% to 74%.

Boiling Point @ 1 atm	20.43°K	-423.0°F	-252.5°C
Freezing Point @ 1 atm	13.98°K	-431.4°F	-259.14°C
Critical Temperature	32.976°K	-399.9°F	
Critical Pressure	12.76 atm		

Compare the boiling point of R-22 refrigerant to the cryogenic fluids listed below.

<u>Gas</u>	<u>Boiling Points</u>	
R-22	-41.4°F	232.4°K
Argon	-297.6°F	87.40°K
Hydrogen	-423.0°F	20.43°K
Oxygen	-297.3°F	90.13°K
Nitrogen	-350.5°F	77.35°K
Helium	-452.1°F	4.26°K
Neon	-410.4°F	27.21°K