

# 1. Temperature and the Ideal Gas Law

(Note: This is a fairly long experiment. To save time, much of the graphing can be done “at home”. As always, make sure that you have all the data you need before you leave.)

## 1.1 Introduction

The most important concept at the foundation of thermodynamics is that of thermal equilibrium. We take this for granted in our daily experiences. We know, for instance, that an ice cube will melt when taken out of the freezer – no matter what object “at room temperature” it is brought into contact with. This is the essence of the utility of temperature and thermal equilibrium: the direction of heat flow is independent of the substance involved - it depends on only temperature. In fact, this defines temperature.

More precise observations of thermal equilibrium are as follows. First of all, as with the equally familiar notion of mechanical equilibrium, we may say that an isolated macroscopic system is in thermal equilibrium, or thermodynamic equilibrium, whenever it attains a state that is not observed to change with time, at least at a macroscopic level. Obviously, for such a situation to occur, it is also necessary that the system in question is in (internal) mechanical and chemical equilibrium.

At the foundations of thermodynamics is the experimental fact that *two systems in thermal equilibrium with a third system must also be in thermal equilibrium with each other*. This is often referred to as the zeroth law of thermodynamics. It is what leads to the empirical notion of a temperature scale. For example, when a mercury thermometer is in thermal equilibrium with one object  $A$ , we can measure the liquid volume of the mercury thermometer. This is a meaningful measure precisely because any other object  $B$ , also in thermal equilibrium with our thermometer in the same state, would be in thermal equilibrium with the first object  $A$ . We will observe, for instance, that heat will not flow between  $A$  and  $B$ . Empirically, the scale of temperature that we ascribe to the thermometer (say, the volume of the mercury) is arbitrary. The temperature of a system is simply a property that determines whether or not it is in thermal equilibrium with other systems. An entirely arbitrary temperature scale, as described above, might be useful for comparing the temperature of your room with its state an hour ago, but it makes for a poor way of communicating observations using totally different temperature sensors. Defining a universal temperature scale is probably one of the most difficult tasks in measurement science. Historically, the procedure was to simply declare by fiat two distinct temperature reference points. For the Fahrenheit scale,  $0^{\circ}\text{F}$  was the temperature of ice mixed with rock salt while  $100^{\circ}\text{F}$  was (approximately) the temperature of the human body. The Celsius scale uses the melting point of ice as the zero point with  $100^{\circ}\text{C}$  defined as the boiling point of water. With either of these two definitions, one can construct a thermometer by simply dividing the difference in expansion of a mercury column by 100 units along the interval between the two temperature extremes.

This opens up the question of what happens when we try to measure temperatures below the freezing point of mercury or above its boiling point. More subtly, if we choose a different thermal sensing liquid, such as alcohol, would the above procedure define the same temperature scale? The answer is: “not exactly”. Liquids and solids don't expand precisely linearly with temperature and such departures would affect a simple dividing scheme. The way out of this morass is to adopt a thermodynamic temperature scale based on the second law of thermodynamics:

$$\Delta S = \frac{\Delta Q}{T} \quad (1.1)$$

where  $\Delta S$  is the change of entropy of a system and  $\Delta Q$  is the corresponding change of its total energy. (See Chapter 21 of Halliday, Resnick and Walker, or Chapter 18 of Young and Freedman.) Operationally, this is a pretty nasty procedure since measuring entropy is not easy to accomplish. The alternative is to use the properties of especially simple physical systems as a secondary standard. The two most accessible are ideal gases (approximated by helium) and black body radiation. The first of these will be explored in this experiment; the second will be the subject of the next assignment.

## 1.2 Thermocouples

Early in the 19th century, Thomas Seebeck discovered that a temperature gradient along a metal wire can cause a current to flow. More specifically, what he observed was that a closed loop, formed of two different wires will maintain a current when the two junctions are at different temperatures. In essence, this “Seebeck effect” can be summarized by a (nearly) linear relationship between the voltage difference  $\Delta V$  and the temperature difference  $\Delta T$  between the ends of a metal wire:  $\Delta V \cong \alpha \Delta T$ . The coefficient  $\alpha$  depends on the metal. The magnitude of  $\alpha$  is fairly small so electric potentials of the order of a millivolt or less are typical. The approximate size of the Seebeck effect can be estimated from the free electron theory of metals. The characteristic conduction electron energy is called the *Fermi energy*,  $E_F$ . In the simplest model,  $E_F$  is given by:

$$E_F = \frac{h^2}{8m_e} \left( \frac{3}{\pi} n \right)^{2/3} \quad (1.2)$$

where  $h$  is Planck's constant,  $m_e$  is the mass of the electron and  $n$  is the conduction electron density. Since metals generally expand when heated, the Fermi energy will decrease slightly with temperature but with different rates for various metals.

For the thermocouple junction shown in Figure 1.1, formed from wires of two different metals (A and B), the voltage difference between the free ends of the thermocouple is approximately proportional to the temperature difference between the junction and free ends:  $V_A - V_B \cong \alpha'(T_J - T_M)$ , where  $T_J$  and  $T_M$  refer to the temperatures of the junction and the leads connected to the meter. The coefficient  $\alpha'$  for the thermocouple depends on the individual Seebeck coefficients  $\alpha_A$  and  $\alpha_B$  for the two metals.

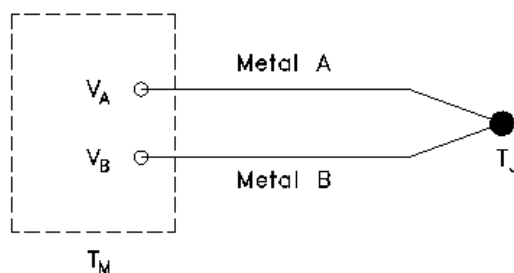


Figure 1.1. Schematic diagram of a thermocouple measurement system

Construct a thermocouple by soldering or twisting together a copper and a constantan wire. Use about 3' of wire – you will need this length to conveniently arrange voltmeters and temperature baths. You will need to strip away about 0.5 inch of insulation at the wire ends to make proper electrical contacts. The copper wire has the familiar reddish tinge; the constantan wire is silvery. You can solder the junction or just twist the pair tightly together with pliers. A Hewlett-Packard model 34401A multimeter operating in voltage mode should be used to measure the voltage difference across the free copper and constantan leads. These potentials are quite low, never more than 10 millivolts.

- Experiment with your thermocouple by measuring the voltage for different temperatures of the junction. For example, warm it up by holding it between your fingers or blowing on it. How large a voltage is produced?
- The input resistance of the multimeter is greater than  $10^7$  ohms. Measure the resistance of the thermocouple wires you are using. How long would they have to be to reduce the measured voltage by say 10%?
- By comparing the voltage readings for two known temperatures, estimate the thermocouple sensitivity. How accurately do you need to measure the voltage to sense a  $1^\circ\text{C}$  temperature change?

The voltage output of a single thermocouple operating alone, is determined by both the temperature of the thermocouple junction and the temperature of the point where it is connected to the voltage-sensing device. Since the latter is not usually well determined, this is not a satisfactory way of accurately measuring temperature (your answer to the previous question should give you some idea of how well you need to know these values). To circumvent this problem, standard practice is to wire two thermocouple junctions in series. One of these junctions is placed in a standard reference bath such as melting ice, while the other junction senses the unknown temperature to be measured. An analogous circuit is shown below in Figure 1.2. If the two batteries shown in the drawing have identical voltages, the voltmeter will read zero. Such a circuit can easily detect small differences in potential between two cells much more accurately than measuring each battery separately. For the task at hand, one can imagine replacing the two batteries with two thermocouples. The potential across the voltmeter is now only a function of the temperatures of the two thermocouple junctions, completely independent of whatever other temperatures are encountered elsewhere in the circuit. Use such a circuit for making the rest of the measurements described below.

This can be accomplished by adding another copper wire to the other end of the constantan wire to make a second junction.

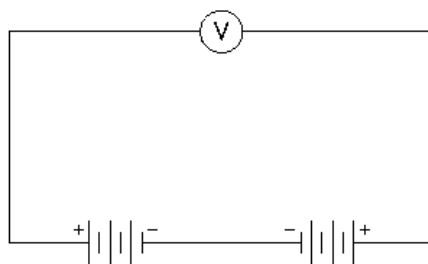


Figure 1.2 Measuring the potential difference of two batteries

Thermocouples must be calibrated, not only because the proportionality constant,  $\alpha$ , is a material-dependent parameter, but also because the linear relationship of voltage to temperature is not strictly satisfied. A number of standard temperature references are used for calibration. A few of these are shown in Table 1.1. To obtain the parameters for a linear relationship two reference points are required. Since the actual voltage-temperature relationship is not quite linear, we will use at least three points: the boiling point of water, the boiling point of nitrogen ( $77.4\text{K} = -195.8^\circ\text{C}$ ), and the freezing point of water, all at atmospheric pressure. Begin with the freezing point of water.

Reference Point	(K)	( $^\circ\text{C}$ )
Triple Point of Hydrogen	13.81	-259.34
Boiling Point of Hydrogen	20.28	-252.87
Triple Point of Water	273.16	.01
Boiling Point of Water	373.15	100.00
Freezing Point of Zinc	692.73	419.58
Freezing Point of Gold	1337.58	1064.43

Table 1.1 A few of the International Practical Temperature Scale reference points

- Prepare a reference temperature bath in which water and ice are well mixed. Using a thermometer, estimate the uniformity of this bath once it has come to thermal equilibrium. Since this will be the reference bath against which other temperatures will be measured, estimate the temperature uncertainty that this bath will introduce into your measurements.
- Determine the voltage reading for boiling water. Exercise care with the electric hot plate. It can produce very nasty burns!
- Also determine the voltage reading for the boiling point of nitrogen. Use a small dewar of liquid nitrogen which you should observe to boil! [*Do not immerse the glass thermometers in liquid nitrogen. It will ruin them.*]

- Determine the voltage reading for ethanol-dry ice mixture at  $-72^{\circ}\text{C}$  if available. (Don't even be tempted to drink the alcohol; it has been “denatured” to make you quite sick!)
- A final calibration point can be determined at room temperature using a thermometer.
- Explain in simple physical terms why the boiling point of a liquid depends on pressure.
- Make a correction to your calibration points due to local atmospheric pressure. You will find a barometer in the lab. Reading the pressure with this device is fairly tricky since it incorporates a vernier scale for higher accuracy. Ask your instructor for help. See Table 1.2 for temperature values of the boiling point of water as a function of ambient pressure. How significant are these corrections?

- Approximately what would the boiling point be at 10,000 feet? (A useful approximate formula for the atmospheric pressure as a function of height is:

$$P = 760.00 \left( \frac{288.15}{288.15 - 0.0065H} \right)^{-5.255877} \quad (1.3)$$

where  $P$  is measured in mm Hg and  $H$  is measured in meters.) At high altitudes,

$$H = \frac{rZ}{r + Z} \quad (1.4)$$

where  $r$  is the mean radius of the Earth, 6370949 meters, and  $Z$  is the height above sea level. (From the CRC Handbook of Chemistry and Physics, page F-141). Use Table 1.3 to interpolate the boiling point of water at a given pressure.

- Plot your data for thermocouple voltage vs. temperature using the spreadsheet program, Excel. You may observe that your four calibration points (including the reference point) do not fall on a straight line. This is not simply experimental error! In order to estimate temperatures other than your reference points, use the following interpolation formula:  $\Delta V = a_1 T + a_2 T^2$  where  $T$  is in Celsius. Determine the coefficients  $a_1$  and  $a_2$  from your calibration data. Excel has facilities for performing these calculations. See Appendix 1.A for useful information about fitting smooth curves to data.
- In order to test your calibration curve, plot it along with about 10 other points taken from the standard copper-constantan thermocouple values provided in Table 1.4. Also, on an expanded scale, plot the difference between the table values and your calibration curve.
- What are the advantages and disadvantages of thermocouples for temperature measurements? Compare with several other kinds of devices that you might find at home or in a lab.

### 1.3 The Ideal Gas Law

Another simple temperature sensing device can be made with a sealed chamber of a gas at low enough density. This is based on the ideal gas law, observed for most gases at densities at or below atmospheric density (see Equation 20-4, HR&W):

$$pV = nRT \quad (1.5)$$

This means that for a fixed volume, the pressure (which can be measured by purely mechanical means) is directly proportional to the temperature. Of course, this is the absolute (Kelvin) scale of temperature. In fact, it is sometimes referred to as the *ideal gas* temperature scale. Thus, you should use the Kelvin scale exclusively for this portion of the lab ( $^{\circ}\text{K} = ^{\circ}\text{C} + 273.15^{\circ}$ ). Ideal gas thermometers may be impractical for laboratory measurement of temperature. However, this portion of the lab will not only serve to illustrate the properties of most gases at low density, but will also provide some familiarity with historical developments in thermodynamics.

- Familiarize yourselves with the operation of the system of valves used to seal off the gauge, the gas reservoir, or to equalize the pressures of the gauge and reservoir. Use the vacuum pump to evacuate the sealed gas bulb and gauge. Calibrate the electronic pressure gauge using the mechanical one by gradually filling the bulb with air to atmospheric pressure. Record simultaneous readings of the electronic and mechanical gauges for at least five different pressure points. Plot readings of electronic gauge vs mechanical gauge. Make a straight line fit to the data.
- To extend the calibration above atmospheric pressure, evacuate the gas reservoir and fill the bulb with nitrogen (or helium or argon) from one of the gas cylinders. It is good practice to flush the tubing with a bit of gas to remove most of the air from the line. Take mechanical and electronic gauge readings at several pressures up to about 18 psi. This will permit raising the temperature of the reservoir without exceeding the range of the pressure gauge.
- Estimate the gas volume of the metal reservoir from the dimensions shown in Figure 1.3. Also estimate the volume of the connecting copper tubing. Comment on the effects of not immersing the entire assembly in a uniform temperature bath.
- Immerse the metal reservoir in three reference temperature baths: ice/water, liquid nitrogen, and boiling water. Immerse the cylinder in the boiling water slowly to reduce the temperature stress. Record the temperatures and gauge readings. Repeat the ice water measurement. This will serve as a check for possible gas leaks.
- Repeat the steps above for all three gases: nitrogen, helium and argon.
- Plot the pressure readings as a function of temperature (in  $^{\circ}\text{K}$ ) for the various gases on a single plot. Using Excel fit each set of measurements to a straight line.

- According to Eq. 1.3, the pressure should be zero when the temperature is zero. Estimate “absolute zero” for each gas by extrapolating your linear plots to  $p = 0$ .
- From Eq. 1.3, a linear dependence is expected. Can you say anything about how *ideal* each of these three gases appears to be? Look up the boiling point of these three gases and see if there is any correlation to the departure from ideal gas behavior.
- The gas in the gauge and connecting tubing is not at the same temperature as the gas in the metal reservoir. For this reason the measured pressure will deviate slightly from strict proportionality with the absolute temperature of the reservoir. Assume the connecting tubing remains at room temperature and derive an expression for the pressure that includes the different temperature of the connecting tubing. (For this calculation, you will need an estimate of the volume of gas inside the tubing and gauge. Samples of the tubing are available in the lab; assume the gauge gas volume is zero.) What can you say about the pressures throughout the system? What physical variable remains constant, independent of temperature, for the system? Estimate how big a correction this would make to your data.
- We have assumed the volume of the stainless steel cylinder is independent of temperature. Look up the temperature coefficient of expansion of stainless steel and estimate how much the volume changes between liquid nitrogen and boiling water temperatures.
- What pressure did you read on the mechanical gauge when it measured actual atmospheric pressure? Based on your measurement of atmospheric pressure with the barometer, what pressure should it have read?

The following conversion factors are useful to relate pressure measurements:

$$\begin{aligned} 1 \text{ Atmosphere} &= 14.69595 \text{ pounds/ sq. in.} \\ &= 760 \text{ mm Hg} \\ &= 29.92126 \text{ inches Hg} \\ &= 101.325 \text{ KiloPascals} \\ &= 1.01325 \text{ Bar} \end{aligned}$$

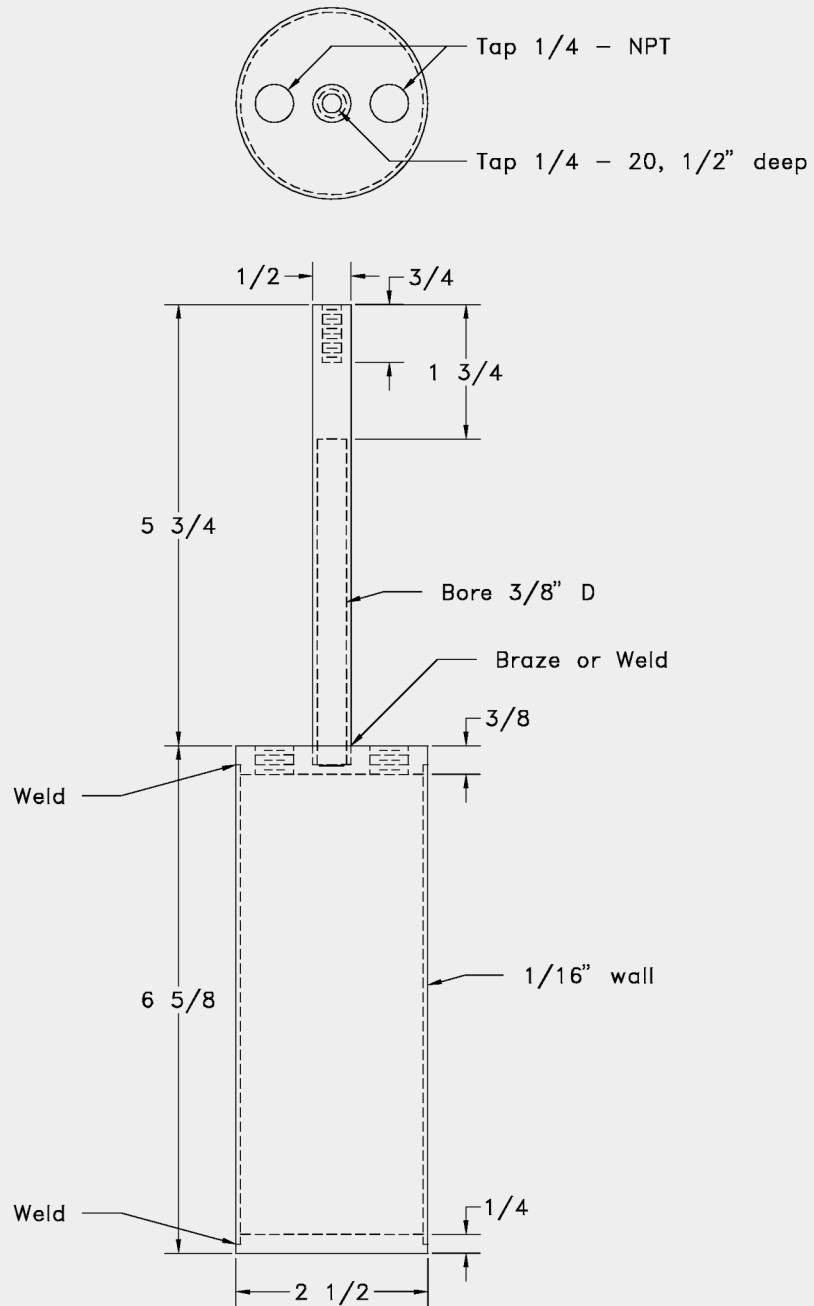
## 1.4 Writing your summary in your notebook

Writing a lab report is one of the most important parts of experimental work. In fact, without a written record, experimental work has no value. All that survives of the experiments of Galileo, or Leonardo da Vinci, or Isaac Newton, is their written accounts, mostly written in their own handwriting in their laboratory notebooks.

Given their prime importance, no wonder lab notebooks intimidate many students. But don't panic. We have some tips to help you write up your work.

- Keep your laboratory notebook with you, and write in it often. Every observation you make should be recorded. I tell my research graduate students that if it isn't in the notebook, it didn't happen. Get into the habit of writing down everything you will need to summarize your results or prepare for the quiz.
- Follow the bullets. The lab manual has tasks denoted in the text by bullets. Typically, each bullet should correspond to some entry in your notebook: some data, or an observation, or a description.
- Use tools during the laboratory. Measurements and analysis often require tools (rulers, microscopes, spectrometers, computers, voltmeters, *etc.*) We have these on hand; use them, and record your measurements by writing them down in your notebook or entering them onto your Excel spreadsheet, for later inclusion in your notebook. The spreadsheet tools are more useful if they are employed during the experiment, not afterwards. If you have a laptop with Excel, you are welcome to use it in the laboratory.
- Plot your data. Remember, a data plot is worth a kiloword. (Or, one word equals one milliplot, or something like that.) Plots made by hand are often more useful than plots made by Excel, because you can understand a trend right away, while you are collecting the data. Often data collection takes some time, *e.g.* letting a thermometer come to equilibrium, so you have time to make a plot while the data are coming in.
- Summarize your findings, right there in your notebook. If you don't know how to do that, we recommend the following simple structure to follow: Question, Method, Answer. The first section describes the goal of the experiment. The second section follows the bullet list recorded in your notebook, with at least one sentence or a brief paragraph for each bullet. The third section summarizes your main findings in a brief statement.





Material: stainless steel  
 All dimensions in inches

gas reservoir
Physics 341
Carl W. Akerlof
April 14, 1997

P (mm Hg)	T (°C)	P (mm Hg)	T (°C)	P (mm Hg)	T (°C)
700	97.714	735	99.067	770	100.366
701	97.753	736	99.104	771	100.403
702	97.792	737	99.142	772	100.439
703	97.832	738	99.18	773	100.475
704	97.871	739	99.218	774	100.511
705	97.91	740	99.255	775	100.548
706	97.949	741	99.293	776	100.584
707	97.989	742	99.331	777	100.62
708	98.028	743	99.368	778	100.656
709	98.067	744	99.406	779	100.692
710	98.106	745	99.443	780	100.728
711	98.145	746	99.481	781	100.764
712	98.184	747	99.518	782	100.8
713	98.223	748	99.555	783	100.836
714	98.261	749	99.592	784	100.872
715	98.3	750	99.63	785	100.908
716	98.339	751	99.667	786	100.944
717	98.378	752	99.704	787	100.979
718	98.416	753	99.741	788	101.015
719	98.455	754	99.778	789	101.051
720	98.493	755	99.815	790	101.087
721	98.532	756	99.852	791	101.122
722	98.57	757	99.889	792	101.158
723	98.609	758	99.926	793	101.193
724	98.647	759	99.963	795	101.264
725	98.686	760	100	794	101.229
726	98.724	761	100.037	796	101.3
727	98.762	762	100.074	797	101.335
728	98.8	763	100.11	798	101.37
729	98.838	764	100.147	799	101.406
730	98.877	765	100.184	800	101.441
731	98.915	766	100.22		
732	98.953	767	100.257		
733	98.991	768	100.293		
734	99.029	769	100.33		

Table 1.2 Boiling point of water as a function of pressure (from the *CRC Handbook of Chemistry and Physics*, 67th edition, page D-183)

T (°C)	P (mm Hg)	T (°C)	P (mm Hg)	T (°C)	P (mm Hg)	T (°C)	P (mm Hg)
0	4.579	27	26.739	53	107.2	79	341
1	4.926	28	28.349	54	112.51	80	355.1
2	5.294	29	30.043	55	118.04	81	369.7
3	5.685	30	31.824	56	123.8	82	384.9
4	6.101	31	33.695	57	129.82	83	400.6
5	6.543	32	35.663	58	136.08	84	416.8
6	7.013	33	37.729	59	142.6	85	433.6
7	7.513	34	39.898	60	149.38	86	450.9
8	8.045	35	42.175	61	156.43	87	468.7
9	8.609	36	44.563	62	163.77	88	487.1
10	9.209	37	47.067	63	171.38	89	506.1
11	9.844	38	49.692	64	179.31	90	525.76
12	10.518	39	52.442	65	187.54	91	546.05
13	11.231	40	55.324	66	196.09	92	566.99
14	11.987	41	58.34	67	204.96	93	588.6
15	12.788	42	61.5	68	214.17	94	610.9
16	13.634	43	64.8	69	223.73	95	633.9
17	14.53	44	68.26	70	233.7	96	657.62
18	15.477	45	71.88	71	243.9	97	682.07
19	16.477	46	75.65	72	254.6	98	707.27
20	17.535	47	79.6	73	265.7	99	733.24
21	18.65	48	83.71	74	277.2	100	760
22	19.827	49	88.02	75	289.1	101	787.57
23	21.068	50	92.51	76	301.4		
24	22.377	51	97.2	77	314.1		
25	23.756	52	102.09	78	327.3		
26	25.209						

Table 1.3 Vapor pressure of water as a function of temperature (from the *CRC Handbook of Chemistry and Physics*, 67th edition, pages D-189-D-190).

EMF values are in millivolts; reference junctions at 0° C; temperatures are in °C. Roeser and Wensel, National Bureau of Standards

T (C)	EMF (mV)	T (C)	EMF (mV)	T (C)	EMF (mV)
-200	-5.54	0	0	200	9.29
-190	-5.38	10	0.39	210	9.82
-180	-5.2	20	0.79	220	10.36
-170	-5.02	30	1.19	230	10.91
-160	-4.82	40	1.61	240	11.46
-150	-4.6	50	2.03	250	12.01
-140	-4.38	60	2.47	260	12.57
-130	-4.14	70	2.91	270	13.14
-120	-3.89	80	3.36	280	13.71
-110	-3.62	90	3.81	290	14.28
-100	-3.35	100	4.28	300	14.86
-90	-3.06	110	4.75	310	15.44
-80	-2.77	120	5.23	320	16.03
-70	-2.46	130	5.71	330	16.62
-60	-2.14	140	6.2	340	17.22
-50	-1.81	150	6.7	350	17.82
-40	-1.47	160	7.21	360	18.42
-30	-1.11	170	7.72	370	19.03
-20	-0.75	180	8.23	380	19.64
-10	-0.38	190	8.76	390	20.25
				400	20.87

Table 1.4 Temperature-EMF values for copper-constantan thermocouples (from the CRC Handbook of Chemistry and Physics, 67th edition, page E-111).

## Appendix 1.A Fitting Curves to Data - the Least Square Method

Often in physics you have a set of  $n$  data points,  $(x_i, y_i)$  for which you would like to find the “best fit” curve that passes as close as possible to all these values. We need to assume the mathematical form this function might have. As an explicit example, we might take the quadratic form:

$$y(x) = A + Bx + Cx^2 \quad (1.6)$$

The task is to find the values for the parameters  $A$ ,  $B$  and  $C$  that makes the residuals,  $\delta_i = y(x_i) - y_i$ , as small as possible. The simplest procedure is to add up all the squared residuals:

$$\Delta = \sum \delta_i^2 = \sum (y(x_i) - y_i)^2 \quad (1.7)$$

This sum is always positive but can be minimized by imposing the following conditions:

$$\frac{\partial \Delta}{\partial A} = \frac{\partial \Delta}{\partial B} = \frac{\partial \Delta}{\partial C} = 0 \quad (1.8)$$

We have thus found three simultaneous equations that must be satisfied:

$$\begin{aligned} \sum (A + Bx_i + Cx_i^2) - \sum y_i &= 0 \\ \sum (A + Bx_i + Cx_i^2)x_i - \sum x_i y_i &= 0 \\ \sum (A + Bx_i + Cx_i^2)x_i^2 - \sum x_i^2 y_i &= 0 \end{aligned} \quad (1.9)$$

These three equations can be rewritten in matrix form as:

$$\begin{pmatrix} \sum 1 & \sum x_i & \sum x_i^2 \\ \sum x_i & \sum x_i^2 & \sum x_i^3 \\ \sum x_i^2 & \sum x_i^3 & \sum x_i^4 \end{pmatrix} \begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} \sum y_i \\ \sum x_i y_i \\ \sum x_i^2 y_i \end{pmatrix} \quad (1.10)$$

Finding the best fit parameters,  $A$ ,  $B$  and  $C$ , requires solving these linear equations, a task for which computers are remarkably adept.

This example can be generalized in two distinct ways. First of all, the equations derived above gave equal weight to each pair of data points. This is usually not quite correct since some data points have larger errors and should affect the computed parameters less severely. The prescription is to introduce a weight,  $w_i$ , for each observation with:

$$w_i = \frac{1}{\sigma_i^2} \quad (1.11)$$

$\sigma_i$  is the estimated standard deviation for the individual measurement. The equivalent matrix equation for fitting quadratic curves is:

$$\begin{pmatrix} \sum w_i & \sum w_i x_i & \sum w_i x_i^2 \\ \sum w_i x_i & \sum w_i x_i^2 & \sum w_i x_i^3 \\ \sum w_i x_i^2 & \sum w_i x_i^3 & \sum w_i x_i^4 \end{pmatrix} \begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} \sum w_i y_i \\ \sum w_i x_i y_i \\ \sum w_i x_i^2 y_i \end{pmatrix} \quad (1.12)$$

These equations could be extended to higher order polynomials simply by increasing the number of rows and columns with the matrix elements formed from successively higher powers of  $x_i$ . Moreover, the model fit function need not even be a polynomial. For example, assume:

$$y(x) = Af(x) + Bg(x) + Ch(x) \quad (1.13)$$

As long as  $f(x)$ ,  $g(x)$  and  $h(x)$  are unambiguous functions of  $x$ , the parameters A, B and C can be computed from:

$$\begin{pmatrix} \sum w_i f^2(x_i) & \sum w_i f(x_i)g(x_i) & \sum w_i f(x_i)h(x_i) \\ \sum w_i f(x_i)g(x_i) & \sum w_i g^2(x_i) & \sum w_i g(x_i)h(x_i) \\ \sum w_i f(x_i)h(x_i) & \sum w_i g(x_i)h(x_i) & \sum w_i h^2(x_i) \end{pmatrix} \begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} \sum w_i f(x_i)y_i \\ \sum w_i g(x_i)y_i \\ \sum w_i h(x_i)y_i \end{pmatrix} \quad (1.14)$$

Note that in all these examples, the least squares matrix is symmetric. This is a consequence of the commutivity of differentiation:

$$\frac{\partial^2 \Delta}{\partial P \partial Q} = \frac{\partial^2 \Delta}{\partial Q \partial P} \quad (1.15)$$

where  $P$  and  $Q$  are any two parameters characterizing the model function,  $y(x)$ . A powerful numerical method for solving such symmetric linear systems is called the Cholesky decomposition. The algorithm for this procedure is extremely robust in maintaining high accuracy in spite of inevitable rounding errors when performing arithmetic operations on floating point numbers. It is also fast. (For details, see *Numerical Recipes in C, The Art of Scientific Computing*, 2nd edition, W.H. Press, S.A. Teukolsky, W.T. Vetterling and B.P. Flannery, Cambridge Press, 1992.).

The linear least squares method described above solves a large fraction of the spectrum of problems encountered in physics but not all. Some problems can be linearized by a trivial transformation:

$$y(x) = Ae^{-Bx} \rightarrow y'(x) = A' + B'x \quad (1.16)$$

where:

$$y' = \log(y(x))$$

$$A' = \log(A)$$

$$B' = -B$$

One is not always so fortunate. A common model function is the Gaussian curve:

$$y(x) = Ae^{-B(x-C)^2} \quad (1.17)$$

The technique shown above won't work here because the  $C$  parameter appears in an intrinsically nonlinear form. For such problems, the solution is trial-and-error guided by intelligent search strategies. Unfortunately, the minimization condition,  $(\partial\Delta/\partial A) = (\partial\Delta/\partial B) = (\partial\Delta/\partial C) = 0$ , is generally not unique and there are no general methods for guaranteeing when you have found the global minimum rather than merely a local one.

## **Appendix 1.B Hints for using the Excel spreadsheet program**

### **Copying cells**

To cut, type Ctrl-X.

To copy, type Ctrl-C.

To paste, type Ctrl-V.

### **Plotting data and curves**

Make sure you enter your data points as numbers, rather than text.

Use the *Chart Wizard* facility to initialize a new graph. It can be accessed via the “bookcase” icon on the top row of the tool bar, near the right-hand end. For *Chart Type*, choose *XY (Scatter)*. You now have a choice of sub-types. The default of unconnected data points is usually the appropriate one for displaying original data. Click *Next*. You now need to indicate the *Data range*. Use the mouse to select the values for the vertical axis, add a comma (,) and then select the values for the horizontal axis. If your data is arranged in columns, click the *Columns* box. Click *Next* to get to the *Data Labels* window and edit according to your taste. For our purposes it is best to choose Major and Minor gridlines on both axes to allow the x,y values to be read more easily. The size of the graphs should reflect the accuracy of your data. Don't use a postage-stamp one if you have 1% data. The next window, *Chart Location*, asks for chart placement. If you want the graph to stand alone, click the *As New Sheet* option, then *Finish*. The choice of axes is rather idiosyncratic: Excel makes the selection based on the position of the data within the spreadsheet.

To add a second set of data, right-click anywhere in the margins of the graph to get a menu containing *Source Data...*. Click this item and in the new window, click *Add* on the left-hand side and then fill in the *X Values:* and *Y Values* boxes appropriately. If this second set of data defines a smooth curve, it would be better to show this as a continuous line instead of

individual points. To do this, right-click any of the data points for the new data and then select *Chart Type ...* from the menu. Select the appropriate sub-type and you're done.

To add error bars to data, right-click any of the data points to get the *Format Data Series...* option. You can then select the *Error Bars* or *X Error Bars* to set the appropriate error values.

### Fitting smooth curves to data

The LINEST function will compute the least-squares coefficients for a polynomial fit to data of the form:

$$y = a_n x^n + a_{n-1} x^{n-1} + \dots + a_1 x + a_0$$

To execute this function, you need to arrange a column (or row) of  $y$ -values and sequential columns (or rows) of  $x$ -values raised to progressively higher powers, i.e.  $(x, x^2, x^3, \dots, x^n)$ . LINEST returns  $n+1$  coefficients plus other statistical stuff, depending on your taste. For this reason, you need to select an appropriate range of cells to contain all these values before entering the actual formula.

The syntax for using LINEST is:

$$= \text{LINEST}(\textit{y-range vector}, \textit{x-range array}, \textit{const}, \textit{stats})$$

[For example, =LINEST(A2:A5,B2:B5,1,1)]

The *x-range array* must include all required powers of the dependent variable. *Const* is a logic value used to indicate whether the  $a_0$  term should be included in the fit or forced to zero. *Stats* should be set to TRUE (1) if the statistical parameters are needed in addition to the fitting coefficients. Since there is no provision for specifying measurement errors, the statistics are fairly worthless. The appropriate cells for the  $y$ -range and  $x$ -range can be selected by dragging over them with the mouse.

Next, select a block of cells for the coefficients and errors. Then make this an array formula by typing Ctrl-Shift-Enter to store in the allocated cells. Note that the return parameters are in the inverse order of the  $x$ -range array columns (or rows).

For most of the graphs in the lab, you can also use the "Add Trendline".

### Obtaining random variables

It is often convenient to have a sequence of random values to help simulate a real physical process. Excel provides a wide variety of statistical distributions using the *Analysis ToolPak*. To obtain this facility, look in the *Tools* menu for *Data Analysis....* If it isn't, there click on *Add Ins...*, click the *Analysis ToolPak* box and then *OK*. From the *Data Analysis...* window, select *Random Number Generation* and then choose whatever options you prefer.



**Experiment 1 - Measurement of Temperature and the Ideal Gas Law****Apparatus List**

Hewlett-Packard model 34401A and 974A multimeters  
Copper and constantan thermocouple wire  
Hot plate  
Large stainless steel beaker  
Two small thermos flasks  
Plastic insulated bucket  
Glass thermometer  
Banana plug terminal adapter for H-P multimeter  
Soldering iron and solder  
Mercury barometer  
Gas reservoir with its attached electronic pressure gauge  
Mechanical pressure gauge  
Gloves for handling LN<sub>2</sub> flask  
Ice, liquid nitrogen  
Wire stripper  
Vacuum pumps and associated plumbing  
N<sub>2</sub>, He and Ar gases  
Dry ice (solid CO<sub>2</sub>) (optional)

