

2.05 The ternary system potassium nitrate / sodium nitrate / water

(4 points)

Outline

An important group of three-component systems¹ comprises those which consist of a mixture of two salts with water. The two salts must have an ion in common, otherwise the system would have four components². Such systems are usually studied isothermally; curves are plotted on triangular co-ordinates representing the conditions of equilibrium of the two solid salts with the ternary liquid. For this purpose a quantitative analysis of many samples of the system must be made. When salts of the alkali metals are involved, analysis is conveniently performed using flame photometry, since alkali metals give bright emission spectra in a region of the spectrum that is easily observed.

Theory

Systems that consist of water together with two salts sharing a common ion are of considerable practical interest. You might think that the phase diagram for such a system would be merely a composite of the phase diagrams for the two binary salt+water systems, but this is not the case since the presence of each salt in solution affects the solubility of the other.

Gibbs' phase rule, one of the simplest of all scientific relations, allows us to calculate the number of phases that can coexist in a mixture of components at equilibrium:

$$F + P = C + 2 \quad (1)$$

¹ A three-component system is known as a "ternary" system.

² A four-component system is a "quaternary" system.

In equation 1, F is the number of degrees of freedom; this is the number of variables such as concentration or temperature that we can adjust independently. P is the number of distinct phases (recall that in many systems there may be more than one solid phase and/or more than one gaseous phase). C the number of (independent) components. It follows that in a ternary system the number of degrees of freedom is $5-P$. These degrees of freedom may be conveniently be taken as temperature, pressure and up to two concentrations.

In order to represent ternary systems graphically, it is normal to work at constant pressure and temperature, so the number of degrees of freedom is then at most 2 (since the number of phases is 1 if we consider only the liquid portion of the system), and the behaviour of the system can be represented graphically in a plane. The method of Gibbs, Bakhuis and Roozeboom uses an equilateral triangle for this representation. The use of triangular diagrams to show the behaviour of ternary systems is discussed in the instructions for experiment 2.06. Using triangular graph paper is simple, but if you need some help, ask a demonstrator.

In this experiment, you will determine the composition of ten equilibrium mixtures containing water, NaNO_3 and KNO_3 . In principle, any method of analyzing for Na^+ and K^+ could be used to find the equilibrium composition. One of the most convenient and simple is that used here: flame atomic emission.

Flame Atomic Emission

If a solution of a salt is aspirated as a mist into a non-luminous flame, the flame takes on a colour characteristic of the metal in the salt (the basis of "flame tests" which you will probably have performed at school). At low salt concentrations, the intensity of the emitted light depends almost linearly upon concentration of metal in the flame so a measurement of the light intensity, which you do in this experiment using a photocell, provides a way of determining the metal concentration. The instrument is calibrated using standard solutions of known concentration.

[Question for your report: at high concentrations, the intensity of emitted light becomes independent of the metal concentration; why is this?]

Procedure

Prepare 10 mixtures of sodium and potassium nitrates in conical flasks of a size which conveniently fits the clamps in the water bath. The total weight of each mixture should be about 10 g, and the concentration range from 100% NaNO_3 to 100% KNO_3 (by weight) must be covered. Be sure to include mixtures in the 95% KNO_3 - 5% NaNO_3 and

95% NaNO_3 - 5% KNO_3 regions. Do not waste time making up mixtures by accurate weighing since the exact composition of the starting mixtures is of no consequence.

Add 7 cm^3 demineralized water from a measuring cylinder to each flask. Set the water bath thermostat to 30°C. Clamp the flasks in the shaker and leave to shake for at least an hour.

While your mixtures are shaking, prepare and measure your calibration standards.

You need to prepare a series of solutions at a concentration that will be appropriate for the photometer, so you must first determine what range of concentration is most suitable. Start by preparing 1 litre of a standard solution containing 0.50g each of KNO_3 and NaNO_3 .

The flame photometer is already connected to gas, compressed air and electricity supplies. Check that the drain tube from the left-hand side leads to the sink; waste liquid from the photometer will dribble from this when it is in use.

1. Turn on the photometer at the mains.
2. The flame is ignited by a high voltage spark produced when the IGNITION button is pushed. Open the gas stopcock by rotating the appropriate knob anticlockwise through 90°. Turn on the gas supply at the tap and push the IGNITION button for a couple of seconds. (If the audible alarm is sounding there is no liquid in the drain pot - stop working and consult the technician.) The gas may take up to twenty seconds to reach the burner, so if the flame does not ignite, wait five seconds and try again.
3. Once the flame is lit, fill a small beaker with demineralized water and place the plastic aspiration tube at the front left of the instrument below the surface of the liquid. Open the circular port at the top left of the front face of the instrument so that you can see the base of the flame.
4. The compressed air stopcock on the front of the photometer should already be open. Check this now before continuing. It should be left open at all times. Cautiously turn on the compressed air at the bench. Gradually increase the pressure so that the flame, which initially will have a large blue ragged central cone, just breaks up into ten small separate cones, one to each burner hole. The pressure of compressed air (as shown on the pressure gauge near the connection to the compressed air line) should be around 0.3 kg cm^{-2} .

5. Turn the filter wheel at the left of the scale on the photometer to bring the Na filter into position. Replace the beaker of water by a beaker containing your standard sodium solution. If the reading goes off scale try changing the Range and Span settings. If you are unable to get a reading on scale, your standard solution is too strong and will need to be diluted.
6. Once you can get the standard solution on scale you need to prepare from it a set of calibration standards. By dilution, prepare a series of solutions covering the range between the concentration of your (possibly diluted) standard and a solution weaker by a factor of ten.
7. Wash the outside of the aspiration tube with a jet of demineralized water. Once more place the beaker of water under the aspirator tube, allow the water to flush out any salt solution, then determine the readings given by each of your diluted standards for both sodium and potassium. (In other words, feed your calibration standard in, record the reading for sodium, then turn the filter wheel and do the same for potassium. Do this for each calibration standard.)
8. Wash, dry and weigh a set of stoppered weighing bottles. Stop the shaking of your mixtures and allow all solids to settle. Pipette 1 cm^3 of the supernatant from one of the mixtures and transfer to a weighing bottle. Stopper and reweigh. (Use a clean dry pipette for each transfer to avoid cross-contamination). Wash out the contents of the weighing bottle into a clean 250 cm^3 flask and make up to the mark. Now withdraw 25 cm^3 from this flask, transfer to a 100 cm^3 flask and again make up to the mark. This is equivalent to diluting the original 1 cm^3 to 1 litre, but requires much less water.
9. Determine the reading given by each sample for both sodium and potassium. .
10. At the end of the experiment, turn off the gas supply to the photometer, then turn off the air supply at the bench (NOT on the instrument). Check the water bath has been turned off. Rinse out the glassware you have used.

Calculations

Tabulate your readings for the sodium standards and construct a calibration curve, showing emission intensity as a function of sodium concentration. Determine and tabulate the concentration of sodium in your samples using the photometer and your calibration curve.

Repeat the procedure to find the concentration of potassium in your samples.

Calculate the percentage compositions of the sample solutions by weight (not forgetting that sodium and potassium are present as their nitrates). Plot and label fully the phase diagram for the system on triangular graph paper (obtain from the service room). Discuss the sources and magnitude of any errors you can identify in the experiment.

Questions

As stated in the instructions, at high concentrations of sodium, the intensity of light emitted by excited sodium atoms in this experiment becomes independent of the metal concentration; why is this?