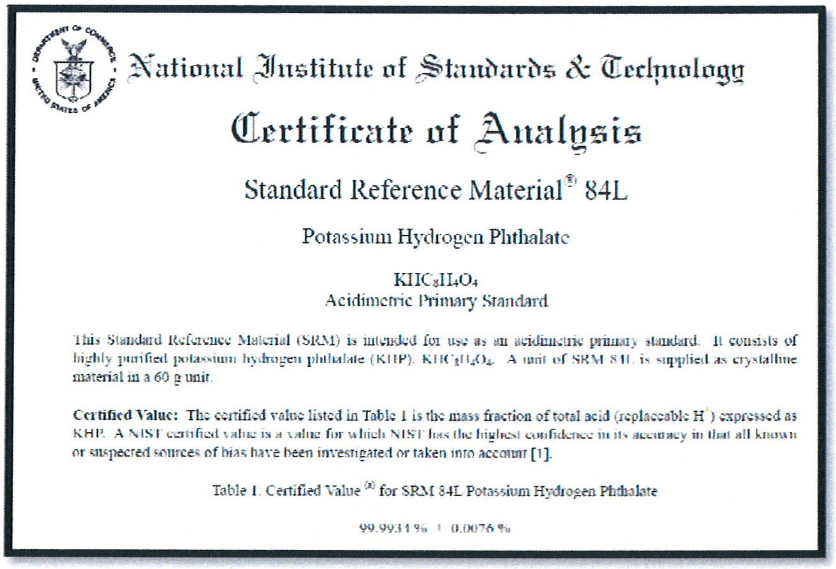
Analytical Crib Oct 20, 2012

Potassium hydrogen phthalate (KHP) is a widely used primary standard (functioning as a monoprotic acid) for acid/base titrations. The titration curve in Table 1 shows an example of using KHP to determine NaOH concentration (a process called standardization). The structure of KHP and its pKa value are also shown in Table 1.

KHP can be obtained with high purity from NIST. Figure 1 shows the certificate of analysis of KHP. The certified value for KHP crystalline material is: 99.9934% ± 0.0076% for 95% confidence level, which is based on results from ***constant current coulometric titration*** of KHP solutions by OH^-. Based on information above, answer questions 1-5.


National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 84L

Potassium Hydrogen Phthalate

$KHC_8H_4O_4$
Acidimetric Primary Standard

This Standard Reference Material (SRM) is intended for use as an acidimetric primary standard. It consists of highly purified potassium hydrogen phthalate (KHP), $KHC_8H_4O_4$. A unit of SRM 84L is supplied as crystalline material in a 60 g unit.

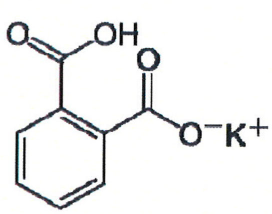
Certified Value: The certified value listed in Table 1 is the mass fraction of total acid (replaceable H^+) expressed as KHP. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account [1].

Table 1. Certified Value [a] for SRM 84L Potassium Hydrogen Phthalate

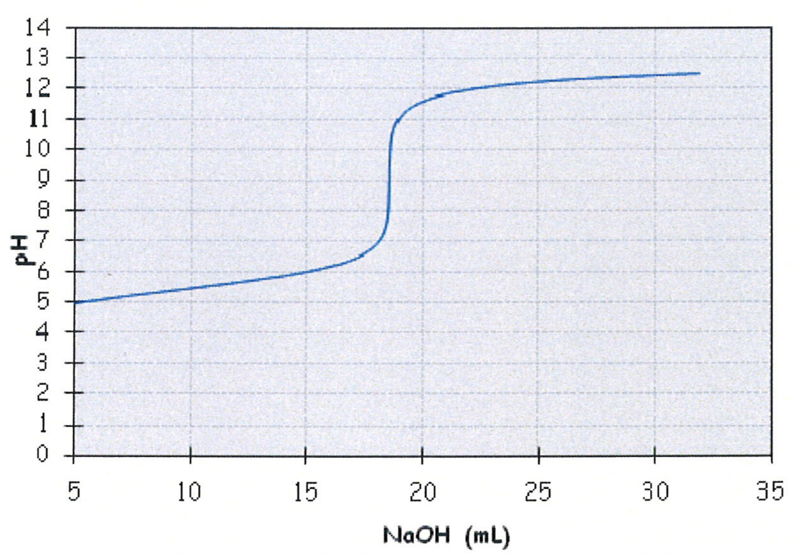
99.9934 % ± 0.0076 %

Figure 1. Certificate of analysis for KHP from NIST.

Table 1. Chemical properties of potassium hydrogen phthalate (KHP) and a titration curve obtained from standardizing NaOH by KHP (0.1000 M and 25.00 ml).



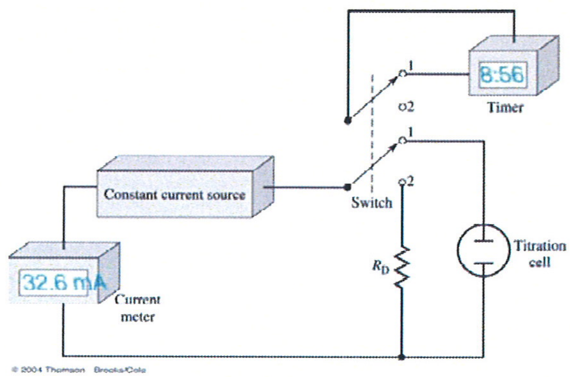
Molecular formula	C8H5KO4
Molar mass	204.22 g/mol
pKa	5.4



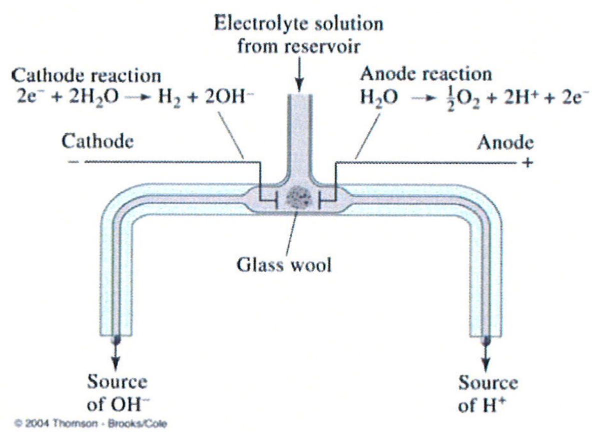
1. [10] Describe the principle of constant current coulometric titration. Limit your answer to 50 words.

In a coulometric titration the titrant is generated electrochemically by constant current from a proper electrolyte. The titrant is delivered into analyte solution. End point detection can be achieved via titration curve or other ways. The quantity of the titrant is obtained according to Farady's law of electrolysis: $n = Q/(F \cdot z)$.

2. [15] Draw an experimental setup for constant current coulometric titration. Label key components in the diagram and briefly explain the corresponding functionalities.



3. [5] Suggest reaction(s) one may use in the electrolytic cell for KHP titration.



4. [10] Comment on why coulometric titrations can be used as a relatively speaking "absolute" method for concentration determination and provide high precision measurements. Limit your discussion to 100 words.

The key to the high precision of coulometric method is that no standardization is needed for NaOH. Instead, its quantity is directly obtained based on Faraday's Laws of electrolysis (n=I*t/(F*z)) via knowing the time and accurate control of current. Given that both time and current measurements can be very precise, columetric titration provides measurements on a "relative" absolute basis.

5. [10] For a constant current of 9.6486 mA, 10.000 s was used to reach the end point for KHP titration. Calculate the quantity of KHP (in moles) in the solution. Show steps and derivations to receive points. Faraday's law of electrolysis: $n = Q/(F \cdot z)$. Q is the total electric charge passed through, *F* is the Faraday constant, 96,485 C mol^{-1}, and *z* is the number of electrons transferred per ion.

1:1 stochiometry of n_e, n_{OH}, and n_{KHP}

$$n_{KHP} = n_e = \frac{Q}{F \cdot z} = \frac{\mathrm{I \cdot t}}{\mathrm{F \cdot z}} = \frac{9.6486 \times 10^{-3}\mathrm{A} \times 10\ \mathrm{s}}{96485\ \mathrm{C \cdot mol^{-1} \cdot 1}} = 1.0 \times 10^{-6}\mathrm{mol}$$

Use the following information, answer questions 6 – 10.

A solution of KHP was prepared at a concentration of 0.1000 M. 25.00 ml of KHP solution was further used to standardize a NaOH solution. The titration curve is shown in Table 1.

6. [10] Calculate the pH of KHP solution before titration. Show derivations to receive points.

$$[H_3O^+] = \sqrt{C_{HA} \cdot K_a} = 6.31 \times 10^{-4} M$$

$$pH = 3.2$$

7. [20] Indicators (HIn) in acid-base titrations are also acid or base themselves. Table 2 lists several commonly used indicators and the corresponding pK_a values. If phenolphthalein was used as an indicator to determine the end point for NaOH standardization, predict the range of NaOH concentrations that might be obtained due to indicator color change. Note that human eyes are only sensitive to color change within concentration ratios of $[In^-] / [HIn] > 0.1$ and $[In^-] / [HIn] < 10$. A zoomed in view of the titration curve is shown in Figure 2.

Table 2. List of indicators	
Indicator	pKa
litmus	6.5
Methyl orange	3.7
phenolphthalein	9.3

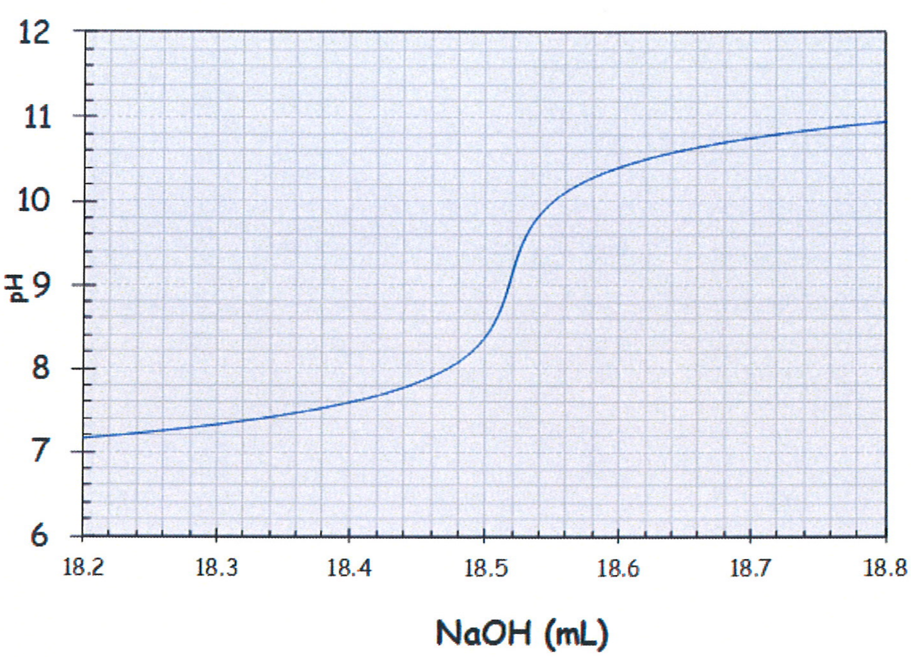


Figure 2. Zoomed-in region of the titration curve in Table 1.

$$HIn + H2O \leftrightarrow H3O^+ + In^-$$

$Ka = \frac{[H3O^+][In^-]}{[HIn]}$ and $[H_3O^+] = \frac{Ka}{[In^-]/[HIn]}$

Take –log from both sides: $pH = pKa + log\frac{[In^-]}{[HIn]}$

Color change range for indicators: $\frac{[In^-]}{[HIn]} > 0.1\ or\ \frac{[In^-]}{[HIn]} < 10$

$$pH = pKa \mp 1$$

For phenolphthalein: pKa = 9.3, color change range: 8.3 to 10.3

Find corresponding V_{NaOH} in Figure 2 → 18.49 ml to 18.58 ml

$$C_{HA}V_{HA} = C_{NaOH}V_{NaOH}$$

$$C_{NaOH,1} = 0.1352\ M,\ C_{NaOH,1} = 0.1346\ M$$

8. [5] If litmus is used as the indicator, comment on the consequence for NaOH standardization. Limit your discussion to 50 words.

If litmus is used, color change range: 5.5 to 7.5

Color change in this pH range will give a lower estimation of V_{NaOH} and therefore a higher estimation of C_{NaOH}.

9. [5] Comment on why the extent of pH change is rather small before the end point (i.e. V_{NaOH}: 5 -15 ml, while it is more dramatic closely around the end point (i.e. V_{NaOH}: 18 -19 ml). Limit your discussion to 50 words.

Before reaching the end point, titration produces buffer solution (HA and A^-) and the pH change is rather small within its buffer capacity. When titration is near the end point, the concentration ratio of A^- and HA is very large, beyond the buffer capacity. This fact leads to a dramatic pH change around the end point.

10. [10] Calculate pH of the solution when KHP is consumed by half. Show derivations to receive points.

$$pH = pKa \mp log \frac{C_{B-}}{C_{HA}} = pKa = 5.4$$

Extra point question:

11. [10] Draw analogies of constant current coulometric titration to volumetric titration. Limit your discussion to 50 words.

Coulometric titrations are in many ways similar to volumetric titrations: the concentration of the titrant is equivalent to the generating current, and the volume of the titrant is equivalent to the generating time.

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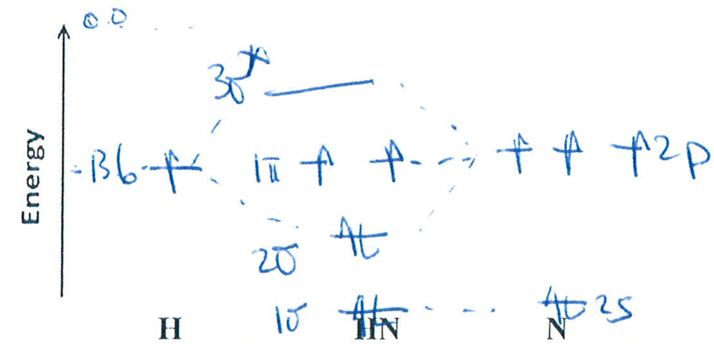
Crib Oct 2012

Inorganic Cumulative Exam

This cumulative exam covers the molecular orbitals of some inorganic systems.

A. (60 points) The first question deals with the diatomic HN molecule.

i. For consistency, use the following valence orbital ionization energies to position the N and H atomic orbitals relative to each other on opposite sides of the page in your answer booklet, organized as in the figure below. In the middle of your diagram, predict approximate energies for the occupied molecular orbitals of the HN molecule. H_{1s} 13.6 eV; N_{2s} 25.6 ev; N_{2p} 13.2 eV. (This means the energy of the H 1s atomic orbital is -13.6 eV, relative to a free electron.) Assume that the internuclear axis defines the z-direction and that the plane of the page is the yz plane.



ii. Connect the MO energy levels with the contributing AO levels, fill in the electrons, and deduce the number of unpaired electrons in the NH molecule.

2 unpaired e⁻

iii. Sketch a contour of the highest energy, *fully* occupied MO, and identify the participating AO's.

$1s_H + 2p_z(N)$

iv. The HN molecule is highly reactive and exists only in the gas phase at high dilution. Using overlap arguments, show that the MO's you found are compatible with dimerization to HNNH, and rationalize the planar molecular geometry of the product as well as any possible isomers.

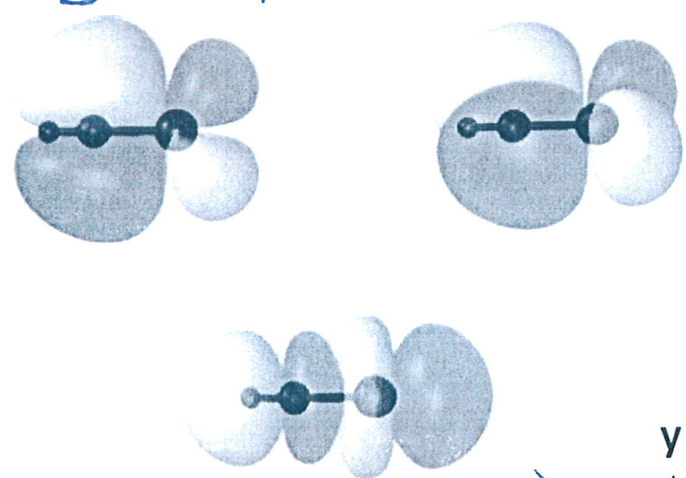
reactive 1π orbitals of NH's σ + π overlap possible and cis isomer

B. (40 points) In the presence of La^+, the HN molecule takes a different path and forms the linear $LaNH^+$ ion (*EJIC* **2012**, 3551). For the purposes of this question, assume that La^+ adopts a $5d^2$ configuration and bonds exclusively via its d orbitals. Assume the d-shell valence ionization energy is about 11 eV. As before, let the z axis be the internuclear axis and let the page define the yz plane. (Continued on next page.)

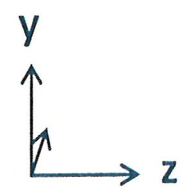
Part B. Continued.

i. The following are crude sketches (contour plots) of the three highest occupied orbitals of $LaNH^+$. Indentify *all* contributing atomic orbitals in each. The dark spheres, the largest being lanthanum, merely identify atom locations.

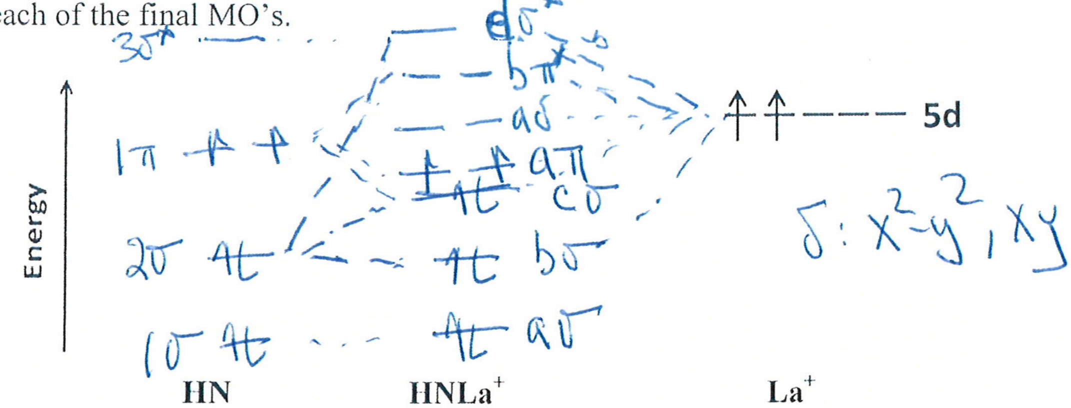
$2p_y(N)\ 5d_{yz}(La)$ $2p_x(N)\ 5d_{xz}(La)$



$2p_z(N)\ 5d_{z^2}(La)$



ii. Draw a MO diagram for $LaNH^+$ organized with the 5d orbitals of lanthanum on the right and the MO's of HN on the left. Connect the MO's of $LaNH^+$ to the appropriate parent orbitals on either side. Assign sigma, pi, or delta symmetry to each of the final MO's.



iii. Finally, show which levels contain electrons in the ground state. Draw an appropriate Lewis structure indicating bonds between adjacent atoms and any lone pairs. Consider only the electrons from the MO diagram. What is the hybridization at N?

La ≡ N – H   sp (N) since Linear

formally sp lone pair → La   sp hybrid orbital binds to H