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Effects of Process Variables on Reaction Mechanisms Responsible for ADUN Hydrolysis, Precipitation, and Gelation in the Internal Gelation Gel-Sphere Process

J. L. Collins
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EFFECTS OF PROCESS VARIABLES ON REACTION MECHANISMS RESPONSIBLE FOR ADUN HYDROLYSIS, PRECIPITATION, AND GELATION IN THE INTERNAL GELATION GEL-SPHERE PROCESS

J. L. Collins, M. H. Lloyd, and R. L. Fellows

Chemical Technology Division

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EFFECTS OF PROCESS VARIABLES ON REACTION MECHANISMS RESPONSIBLE FOR ADUN HYDROLYSIS, PRECIPITATION, AND GELATION IN THE INTERNAL GELATION GEL-SPHERE PROCESS

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ABSTRACT

Studies were conducted that indicate five chemical reactions are important during acid-deficient uranyl nitrate (ADUN) hydrolysis and precipitation in the internal gelation process for microsphere preparation. Experiments performed to determine pH profiles during urania gelation in conjunction with hexamethylenetetramine (HMTA) decomposition experiments were useful in defining important characteristics of these reactions and in determining process variables that affect reaction rates as well as pH regions in which ADUN precipitates. These variables are the nitrate-to-uranium and the HMTA-to-uranium mol ratios, the uranium concentration, and the gel formation temperature. The influence of these process variables on the solution pH and precipitation reactions is discussed. The results of this study suggest that increased knowledge of these reactions and their kinetics should make it possible to better understand and control microsphere characteristics, which can vary widely with variations in process variables. It is this inherent capability to produce metal oxide microspheres with precise properties that makes internal gelation processes uniquely useful for many applications.

1. INTRODUCTION

This study was conducted in support of the Direct Press Spheroidized (DIPRES) process,[1,2] which employs internal gelation techniques to produce $(U,Pu)O_2$ microspheres for use as direct-press feed for fast breeder reactor (FBR) pellet fabrication. The major objectives were to define and better understand the principal reactions that occur during ADUN hydrolysis, precipitation, and gelation and to determine the effects of process variables on these reactions. A secondary objective was to determine the pH at which precipitation and gelation occur as a function of key process variables.

An internal gelation process for preparing UO_2 microspheres was originally developed at the KEMA laboratories, located in the Netherlands.[3] Since that time, various modifications of the process have been evaluated and utilized in a number of laboratories throughout the world.[4-9]

In common with all such processes, concentrated metal nitrate feed solutions are prepared, cooled, and mixed with cold concentrated solutions of HMTA and urea to form a broth that can be dispensed as droplets into a hot medium in which gelation occurs. The gel spheres are then collected and washed in NH_4OH solution to remove NH_4NO_3, urea, and unreacted HMTA prior to drying.

Previously reported descriptions of internal gelation processes have almost exclusively described UO_3 precipitation as resulting from the hydrolysis of ADUN with ammonia produced by the temperature-induced decomposition of HMTA.[3,6,9-12] The present study shows that while this reaction can occur, the overall behavior is much more complex and that at least five principal reactions are involved in ADUN hydrolysis and precipitation. The study also suggests that an increased understanding of these reactions and their kinetics should facilitate control of the product characteristics, which can vary widely with variations in process parameters. It is this inherent capability to produce metal oxide microspheres with precise properties that makes these processes uniquely useful for many applications.

2. EXPERIMENTAL

The experiments in this study were designed to duplicate as closely as possible the typical procedures used in sol-gel microsphere formation.

Stock solutions of ADUN were prepared by partially neutralizing uranyl nitrate with NH_4OH to give NO_3^*/U mol ratios of 1.50 to 2.00. (See Sect. 3.1 for the definition of the term NO_3^*/U mol ratio.) The uranium concentration of each solution was 1.84 M. A stock solution of HMTA and urea was prepared in which each component concentration was 3.1 M.

The apparatus consisted of an ice bath, a hot-water bath, a Beckman model 3550 digital pH meter with a Corning combination electrode and a thermocompensator, and a recorder.

In each experiment, solutions of ADUN feed (1 mL) and HMTA were chilled and thoroughly mixed in 12-mL centrifuge tubes in an ice bath. The pH electrode was then inserted into the solution. At the same time, the thermocompensator was similarly placed in a 12-mL centrifuge tube containing ~2 mL of chilled water. After allowing time for temperature and pH equilibrium (~3 to 5 min), both tubes were simultaneously transferred to the hot-water bath and maintained there for ≥10-min periods to effect gelation. During this period, the pH was continuously recorded and the gelation induction time was noted.

To ensure accuracy of measurement, a buffer solution of pH 4.00 (potassium acid phthalate; M = 0.05) was measured at the bath temperature both prior to and after testing. Table 1 shows how the pH of the buffer solution varied with temperature. Our measurements are compared with those reported by Bates[13] previously.

Table 1. Variation of pH of buffer solution with temperature

Source of pH value	Temperature (°C)									
	0	10	20	30	40	50	60	70	80	90
Bates[a]	4.003	3.998	4.002	4.015	4.035	4.060	4.091	4.126	4.167	4.205
ORNL	3.99	4.00	4.00	4.02	4.04	4.06	4.10	4.13	4.17	4.21

[a]R. G. Bates, Determination of pH; Theory and Practice, 2nd ed., Wiley, New York, 1973, p. 73.

3. RESULTS AND DISCUSSION

Previous descriptions of internal gelation sol-gel processes (see Sect. 1) have almost exclusively described UO_3 precipitation as being due to the reaction of ADUN with ammonia that is produced by the temperature-induced decomposition of HMTA.

Results of the studies to be described in this report show that five principal reactions are involved in the hydrolysis and precipitation of uranyl nitrate hexahydrate (UNH) and that the kinetics of four of these reactions vary with temperature. It is undoubtedly this complexity and the concomitant effects on the crystallite morphology of the precipitated urania phase that result in the widely different product characteristics that are observed with variations in key process variables.[1]

The five reactions can be shown as follows:

decomplexation,

$$UO_2(NO_3)_2 \cdot Urea \xrightarrow{Heat} Urea + UO_2(NO_3)_2 \; ; \tag{1}$$

hydrolysis,

$$UO_2^{2+} + 2H_2O \xrightarrow{Heat} UO_2(OH)_2 + 2H^+ \rightarrow UO_3\downarrow \; ; \tag{2}$$

HMTA protonation,

$$(CH_2)_6N_4 + H^+ \rightarrow [(CH_2)_6N_4H]^+ \; ; \tag{3}$$

HMTA decomposition,

$$(CH_2)_6N_4 + 6H_2O \xrightarrow{Heat} 4NH_3 + 6CH_2O \; , \tag{4a}$$

$$UO_2^{2+} + 2NH_4OH \rightarrow UO_2(OH)_2 \rightarrow UO_3\downarrow \; ; \tag{4b}$$

Monomethylol urea formation,

$$CH_2O + Urea \xrightarrow{Heat} NH_2\text{-}CO\text{-}NCH_2\text{-}OH \; . \tag{5}$$

The results clearly show that temperature-induced ADUN-urea decomplexation and ADUN hydrolysis are the initiating reactions during urania precipitation and gelation. Recognition of this behavior makes it obvious that

the gelation temperature and the acid deficiency of the uranium salt must significantly affect the precipitation rate because (1) both decomplexation and hydrolysis are strong functions of temperature, and (2) the degree of acid deficiency affects the total concentration of hydrogen ion produced during hydrolysis.

A second important behavior that has not been generally recognized is HMTA protonation, which effectively removes H^+ from the solution. This reaction has been determined to be generally more significant than HMTA decomposition. In fact, these studies indicate that HMTA decomposition does not occur until almost all the HMTA is protonated, even at temperatures as high as 90°C. Consequently, HMTA decomposition does not appear to be involved in uranyl nitrate hydrolysis when the feed broths have high HMTA/U and low NO_3^-/U mol ratios; at nearly all feed conditions of interest, most ($\geq$70%) of the H^+ is neutralized by the HMTA protonation reaction rather than by the HMTA decomposition reaction. The HMTA/U mol ratio affects both the initial feed broth pH at 0°C and the pH profile during precipitation, primarily because of HMTA protonation.

It has been generally recognized that urea is essential for feed broth stability because it forms a stable complex with the uranyl ion at ~0°C. This behavior is supported by the present study, and a second significant role of urea was recognized, namely, that urea accelerates the rate of protonated HMTA decomposition. This acceleration appears to be due to the reaction of CH_2O with urea, which forms monomethylol urea.[14]

In this study, it was not possible to rigorously determine the effects of temperature on the various reaction rates or to address uranium polynucleation phenomena associated with hydrolysis, both of which are potentially important for understanding uranium precipitation behavior. However, the results do provide information that is a necessary first step in understanding the effects of process variables on microsphere product characteristics.

3.1 HYDROLYSIS OF ADUN SOLUTIONS AND THE EFFECTS OF PROCESS VARIABLES

The acidic pH condition of either a UNH or an ADUN solution results from the uranyl hydrolysis reaction

$$UO_2^{2+} + HOH \rightleftharpoons UO_2(OH)^+ + H^+ .$$

The $UO_2(OH)^+$ has a tendency to form the $(UO_2)_2(OH)_2^{2+}$ dimer.[15,16] The degree of dimerization is dependent on the pH, the concentration, and the temperature of the solution. Typically, the pH of an ADUN solution at uranium concentrations of interest is in the range of 2 to 3 at 25°C, and UO_3 precipitation normally occurs when the pH increases to values in the range of 3.5 to 4.0. Three factors — the NO_3^-/U mol ratio, the solution temperature, and the uranium concentration — can affect this equilibrium and are reflected by changes in the solution pH as changes in H^+ occur.

The initial uranium solution that is mixed with HMTA to form the feed broth is usually acid deficient in the internal gelation process. Solutions of ADUN can be prepared in several ways, such as by dissolution of UO_3 or U_3O_8 in a substoichiometric amount of HNO_3 or by amine extraction of nitric acid from stoichiometric UNH. The resulting uranium solution is substoichiometric in nitrate; and since this is an important process variable, it is convenient to describe the feed solution in terms of the NO_3^-/metal mol ratio. Stable ADUN feeds can be prepared at high uranium concentrations at any NO_3^-/U mol ratio within the range of 1.50 to 2.00.

In essence, a substoichiometric NO_3^-/U mol ratio is equivalent to prehydrolysis of the uranyl ions in the UNH solution. For example, uranyl hydrolysis in an ADUN solution with a NO_3^-/U mol ratio of 1.5 can be shown as follows:

$$2UO_2(OH)_{0.5}(NO_3)_{1.5} + 3H_2O \xrightarrow{\text{Heat}} 2UO_2(OH)_2 + 3HNO_3 ,$$

$$2UO_2(OH)_2 \rightarrow 2UO_3 \cdot 2H_2O\downarrow .$$

The complete conversion to $UO_2(OH)_2$ can be accomplished more rapidly with substoichiometric UNH because there is less HNO_3 to be removed or neutralized.

Uranyl nitrate can also be made acid deficient by partial hydrolysis of the uranyl ions with NH_4OH without incurring any significant variation in feed characteristics or subsequent processing behavior. However, in this method, nitrate is not actually removed from the system and the term NO_3^-/U mol ratio becomes ambiguous.

In the study presented here, ADUN solutions were prepared by prehydrolysis with NH_4OH and the term NO_3^*/U mol ratio is used to reflect only the nitrate associated with unhydrolyzed uranyl nitrate and not that associated with NH_4NO_3, which is also formed (mol total nitrate minus mol NH_4OH added). It has precisely the same significance as the NO_3^-/U ratio in ADUN solutions that are actually substoichiometric in NO_3^-.

Figure 1 illustrates the effects of the temperature and the NO_3^*/U mol ratio on the pH of ADUN solutions that were 0.92 M in uranium. The linear decrease in pH (increased hydrolysis) as a function of increasing temperature is shown for two solutions with NO_3^*/U mol ratios of 1.60 and 1.90. This decrease is in very good agreement with data reported by Botts et al.[17] (also shown in Fig. 1) for an NO_3^-/U mol ratio of 1.56.*

The effect of the NO_3^*/U mol ratio on the pH of ADUN solutions at 25°C is also shown in Fig. 1. A regular increase in pH occurs with decreasing NO_3^*/U mol ratios. Data reported by Botts are also shown for ADUN solutions with NO_3^-/U mol ratios of 1.60, 1.70, 1.80, and 1.90. The excellent agreement demonstrates that the method of adjusting the ratio does not significantly alter the pH levels of ADUN solutions.

The effect of uranium concentration, which is the third important variable affecting the pH of ADUN solutions, is shown in Fig. 2, where the uranium concentrations were varied from 0.92 to 2.6 M for solutions with NO_3^*/U mol ratios at 1.60 and 1.80. As shown, the pH decreased as the uranium concentration was increased. Figure 3 shows the dual effect of varying the NO_3^*/U mol ratio of uranium solutions with metal concentrations

---

*Their ADUN stock solutions were prepared by dissolving UO_3 in concentrated HNO_3. Each of the initial solutions had an NO_3^*/U mol ratio of 1.56. Weighed amounts of 2.0 M HNO_3 were added to make the solutions with higher ratios.

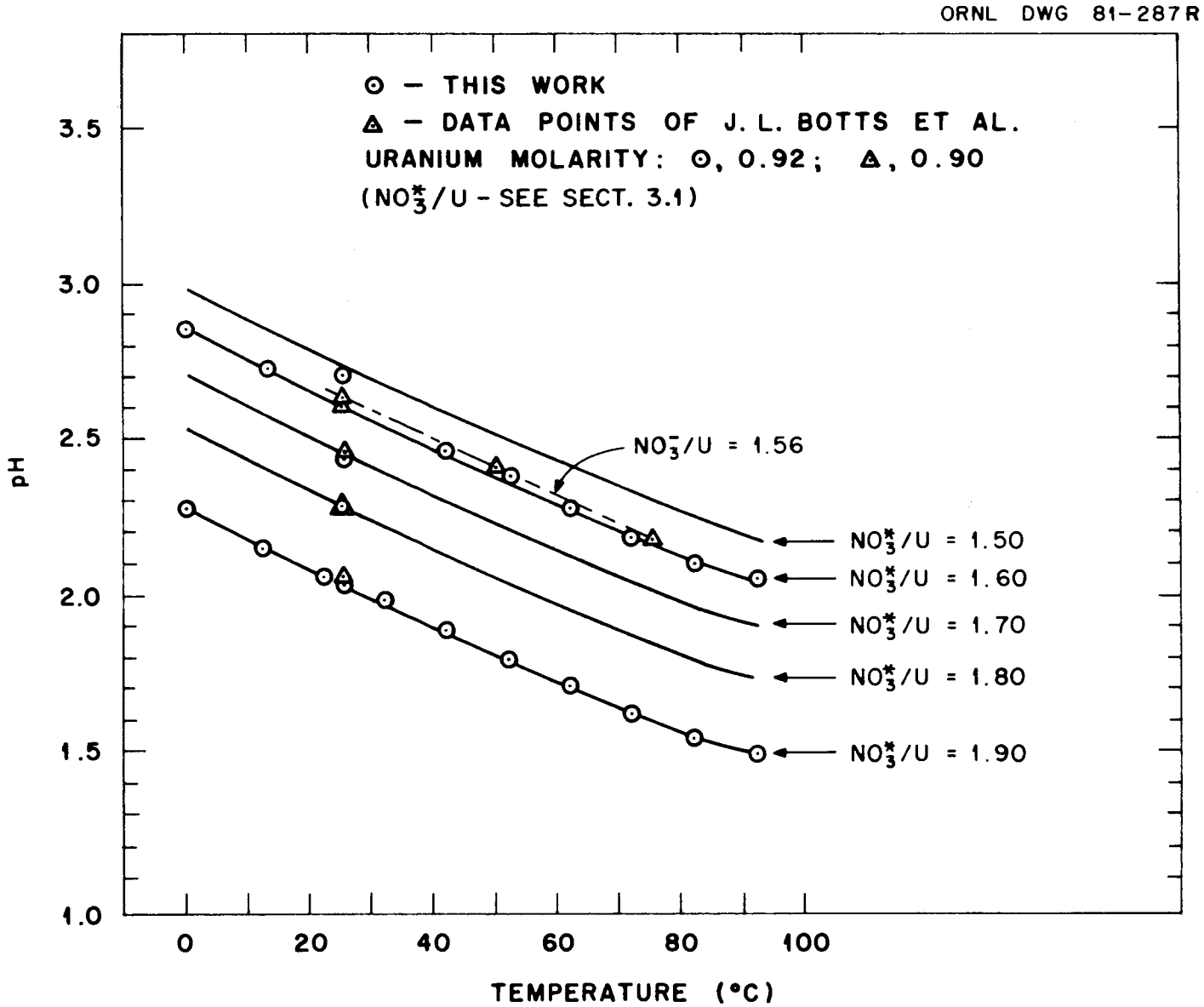

Fig. 1. Effect of NO_3^*/U mol ratio on uranyl nitrate solution pH as a function of temperature.

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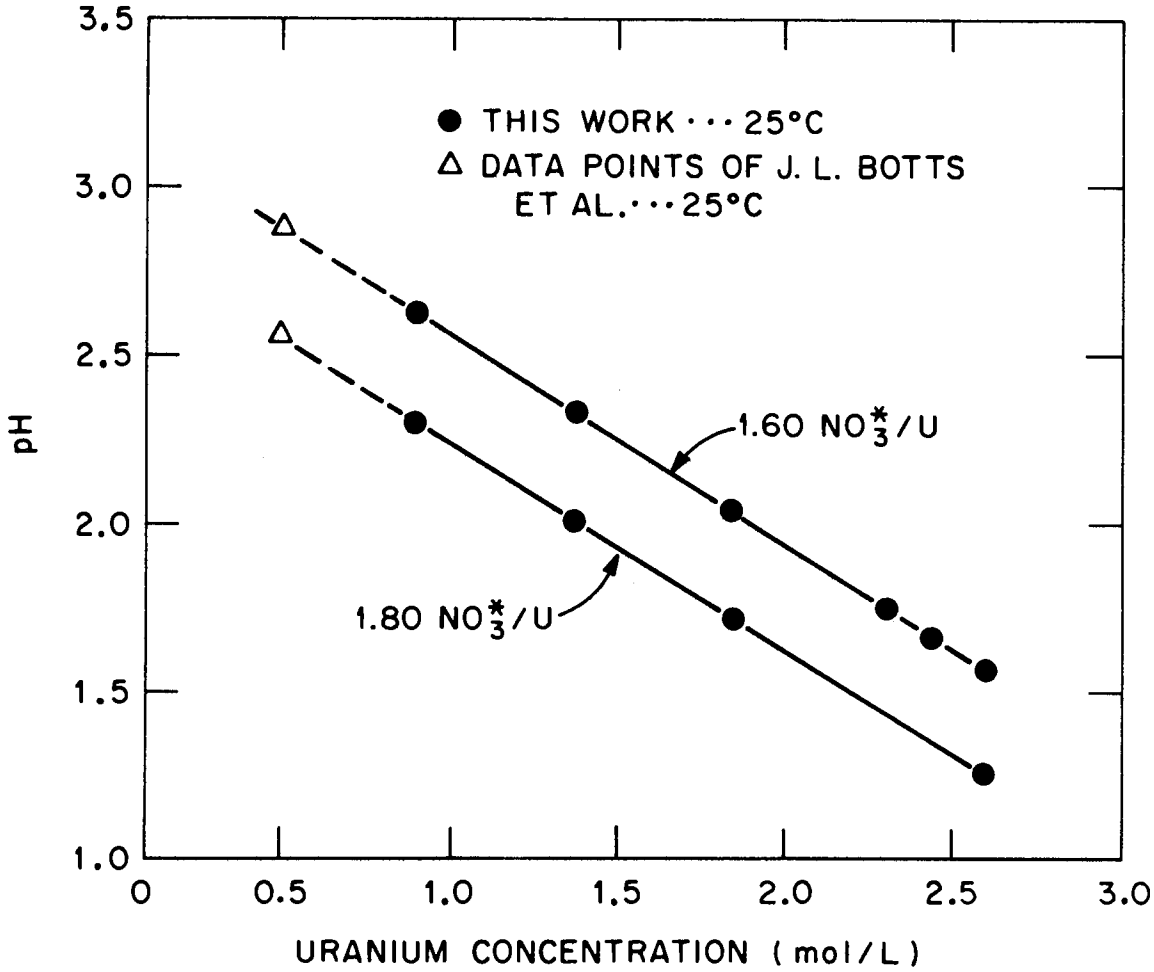

Fig. 2. Effect of uranium concentration on pH of ADUN solutions.

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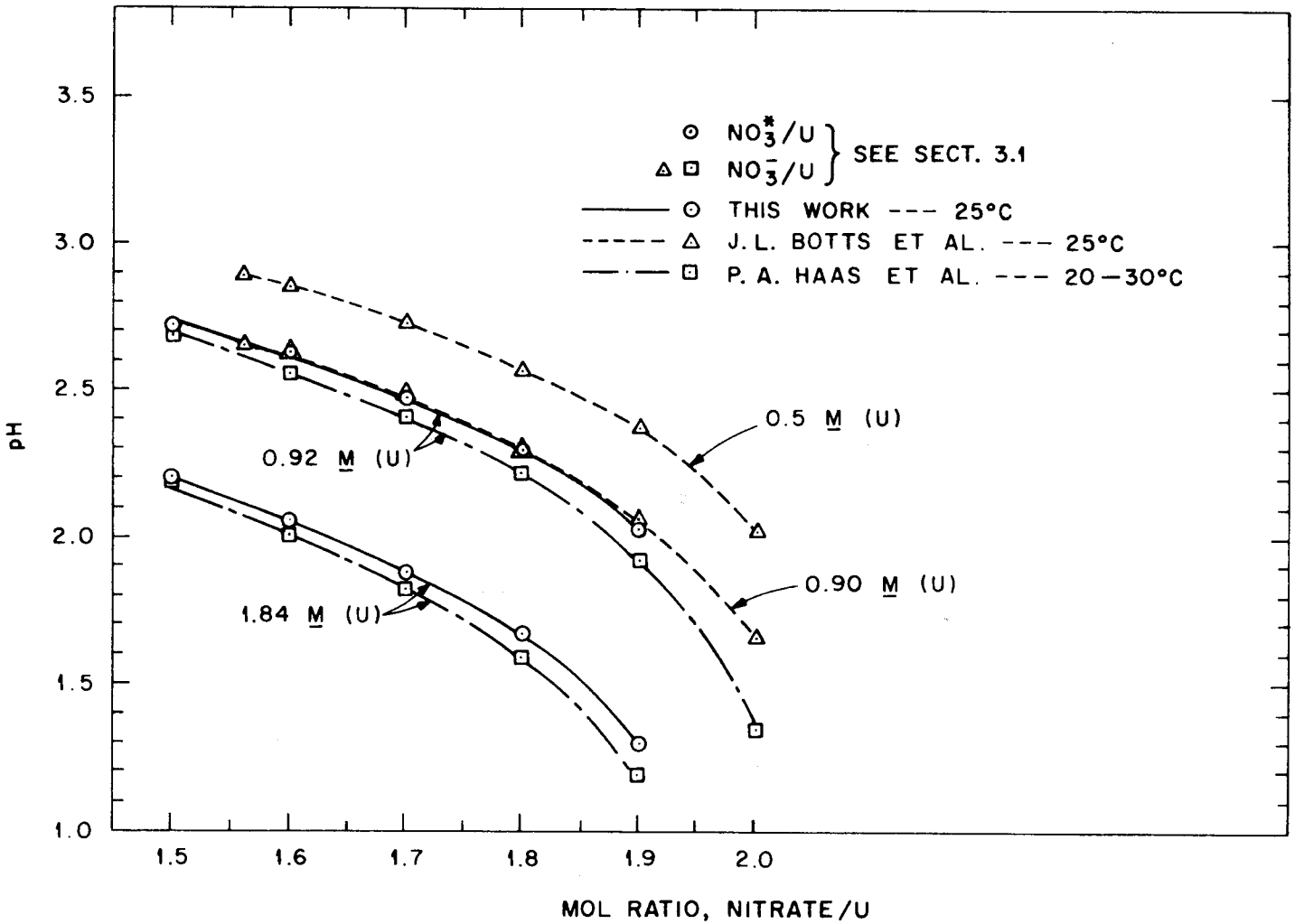

Fig. 3. Effect of uranium concentration on uranyl nitrate solution pH as a function of NO_3^*/U mol ratio.

of 0.92 and 1.84 at a constant temperature of 25°C. Again for comparison, pH data are shown in Figs. 2 and 3 for results reported by Botts et al.[17] and by Haas[9] for comparable NO_3^-/U mol ratios and metal concentrations.

Based on the effects of the three variables previously described, it was found that the pH of an ADUN solution can be empirically determined by the following equation:

$$pH = 5.79 - 1.505(NO_3^*/U) - 0.0091(T) - 0.598(U),$$

where

(NO_3^*/U) = mol ratio (1.50 through 1.80),
(T) = temperature (0 to 80°C),
(U) = concentration (0.50 to 1.84 mol/L).

The linear behavior shown in Fig. 1 for NO_3^*/U mol ratios of 1.50, 1.70, and 1.80 were calculated using this equation.

3.2 EFFECTS OF PROCESS VARIABLES ON pH OF FEED BROTH

A concentrated ADUN solution is cooled to 0°C and mixed with a concentrated solution of HMTA and urea to form the feed broth in the internal gelation process. The pH of this broth at 0°C is influenced singificantly by the variables affecting the pH of the ADUN solution and also by the HMTA/U mol ratio.*

The pH values determined for feed broths at 0°C as a function of the HMTA/U mol ratio for NO_3^*/U mol ratios in the range of 1.50 to 2.00 are shown in Fig. 4. In one set of experiments, a solution that was 3.1 M in HMTA and urea was added incrementally to two ADUN solutions with the same initial uranium concentration (1.84 M) but with different NO_3^*/U mol ratios (1.60 and 1.90). The pH of the broth increased significantly as the HMTA/U mol ratio increased at each NO_3^*/U mol ratio, as indicated in

*In all the experiments reported here, broths were prepared with HMTA solutions that contained an equal concentration (molarity) of urea. However, when the HMTA/U ratio is discussed as a process variable, the corresponding urea concentration will not be noted because the effect of urea is not comparable to the effect of HMTA as a process variable (see Sect. 3.5).

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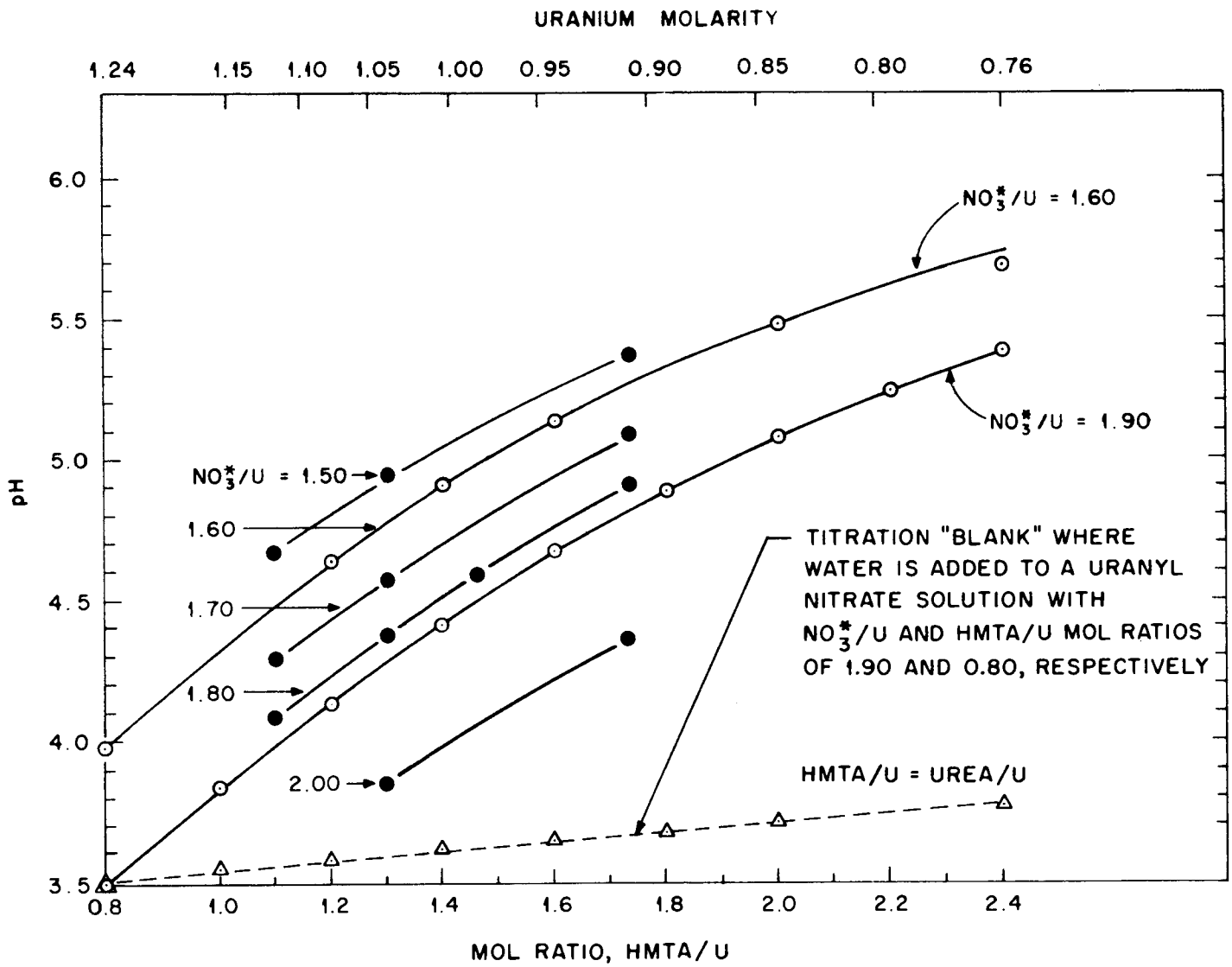

Fig. 4. Effect of HMTA/U mol ratio on pH of the feed broth as a function of NO_3^*/U mol ratio at 0°C.

Fig. 4. In these experiments, the uranium concentration decreased as the HMTA/U ratio was increased. [The change in uranium concentration (molarity) is shown at the top of the graph in Fig. 4.] Since the pH of the broth increased as the uranium concentration was decreased (see Fig. 2) and also as the HMTA/U mol ratio was increased, an experiment was conducted in which only the uranium concentration was varied (see the bottom curve of Fig. 4). These data show that ~13% of the net pH increase was due to the uranium dilution effect at the NO_3^*/U and HMTA/U mol ratios indicated.

Precipitation of UO_3 would be expected in most cases in the broth pH range indicated (3.5 to 5.7); precipitation always occurs if the broths are prepared without urea. The broths are stabilized by adding urea to complex UO_2^{2+} (see Sect. 3.5). The stability of this complex, which is temperature dependent, decreases rapidly with increasing temperature.

The pH values for the feed broths are significantly higher than those for comparable ADUN solutions that do not contain HMTA. This increased pH results primarily from the tendency for HMTA to be protonated, as shown by the following reaction:

$$(CH_2)_6N_4 + H^+ \rightleftarrows [(CH_2)_6N_4H]^+ .$$

Based on this reaction, the broth pH would be expected to increase with increasing HMTA/U mol ratio; however, it will be shown subsequently (Sect. 3.3) that the high pH observed at 0°C is not due either to HMTA decomposition or to the presence of urea.

3.3 pH PROFILE DURING PRECIPITATION AND GELATION OF ADUN

The profile obtained when the pH of a feed broth is recorded continuously as the broth is heated from 0°C to the desired temperature provides significant insight into the role of ADUN hydrolysis as well as other reactions involved in precipitation and gelation.

A typical profile is presented in Fig. 5. The lower curve shows the pH of the feed broth as a function of time, while the upper curve shows

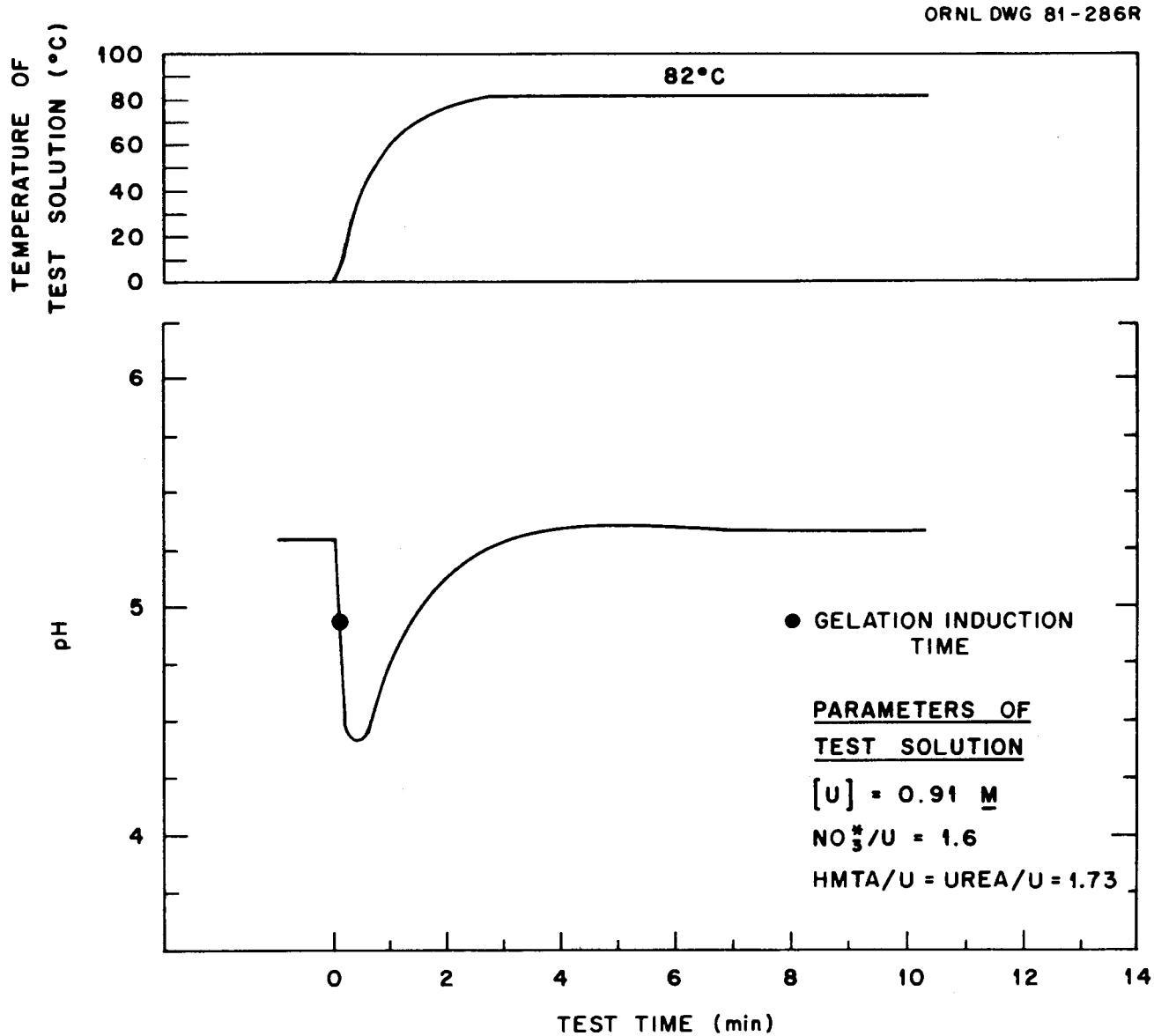

Fig. 5. Profile showing pH vs time for a feed broth solution heated in the manner indicated by the temperature—vs—time profile.

the corresponding temperature of the feed broth while being heated in a water bath. Curves such as this provide evidence that the initial reactions occurring involve ADUN-urea decomplexation and temperature-induced hydrolysis of the UO_2^{2+} ion, because hydrolysis is the only reaction that can generate H^+ and the corresponding rapid decrease in pH:

$$UO_2 \cdot (urea) + 2HOH \xrightarrow{Heat} UO_2(OH)_2 + urea + 2H^+ .$$

The subsequent increase in pH results from either the protonation or the decomposition of HMTA, or both. (These reactions are discussed in Sect. 3.4.)

The solid circle shown on the pH curve in Fig. 5 indicates the time at which UO_3 precipitation began. Since UO_3 precipitation would be expected to occur throughout the entire pH range shown without the stabilizing effect of urea complexation of UO_2^{2+}, this point should primarily reflect the temperature at which significant decomplexation occurs.

It will be shown in Sect. 3.4 that pH profiles not only define variations in pH during UO_3 precipitation as a function of key process variables, but also provide qualitatively useful insight regarding variations in reaction rates as a function of process variables.

3.4 ROLE OF HMTA — PROTONATION vs DECOMPOSITION REACTIONS

Although HMTA protonation reactions are known to occur, the importance of this reaction in UO_3 precipitation behavior in internal gelation processes has not been previously recognized or understood.

Decomposition reactions of HMTA have been described by Tada,[18] who showed that molecular HMTA does not react as such and that $(CH_2)_6N_4H^+$ is the reacting species according to the equation

$$(CH_2)_6N_4 \cdot HCl + 3HCl + 6H_2O \rightarrow 4NH_4Cl + 6HCHO .$$

Tada also showed that the initiating reaction (protonation) involves salt formation:

$$(CH_2)_6N_4 + HCl \rightarrow (CH_2)_6N_4 \cdot HCl .$$

Our studies indicate that precisely comparable reactions occur in the HNO_3-HMTA system. The lower curve (A) in Fig. 6 demonstrates the distinctive equivalence point that is obtained when HMTA is titrated with HNO_3 at 25°C. This results from the following reaction:

$$(CH_2)_6N_4 + HNO_3 \rightarrow (CH_2)_6N_4 \cdot HNO_3 .$$

The end point in such a titration provides a quantitative determination of the HMTA molarity.

From the well-defined protonation end point, it is clear that HMTA decomposition did not occur during this titration. In fact, the stability of the pH value after 25 mL of titrant had been added (the pH did not vary in 20 min) demonstrates that HMTA·HNO_3 salt was not detectably decomposed at 25°C even in the presence of somewhat excess HNO_3 (equivalence point = 18.3 mL). However, Tada's[18] experiments confirmed that HMTA decomposition does occur at higher acid concentrations. Detectable decomposition of HMTA also occurs when HMTA is in the presence of urea (curve B, Fig. 6). Decomposition is easily detectable by a change in pH behavior beginning near the equivalence point. In this experiment, a solution that contained the same concentration of HMTA as used in the previous experiment plus an equivalent molarity of urea was titrated with HNO_3 at 25°C.

As shown in Fig. 6, the titration curves were essentially identical until almost an equivalent amount of HMTA had been protonated (~95% as estimated from curves A and B). During the protonation of HMTA with HNO_3 at 25°C, pH equilibrium was established rapidly after each addition of acid. In the example shown, acid additions up to a volume of 17.4 mL (95% of the end-point amount) resulted in very rapid pH equilibrium, whereas subsequent acid additions resulted in an initial decrease in pH followed by a very slow increase in pH due to the slow decomposition of protonated HMTA. The last three points shown were the pH values obtained after equilibration times of 10 min; they resulted in a relatively constant pH value of 3.8, which correlates with the volume of acid (17.3 mL) consumed during the protonation reaction.

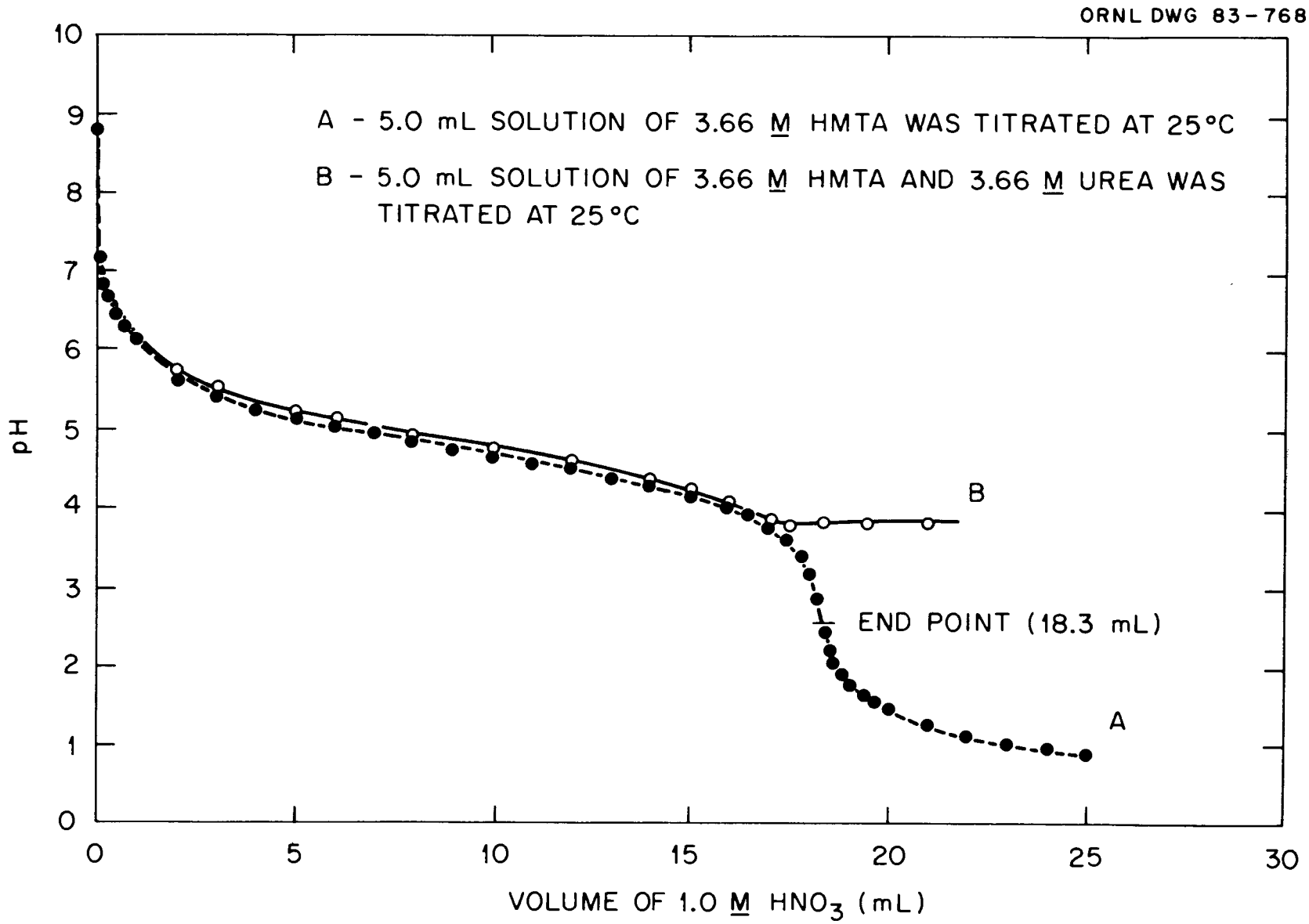

Fig. 6. Potentiometric titrations of concentrated HMTA solutions without (A) and with (B) urea at 25°C.

The effect of urea on HMTA decomposition is a temperature-dependent phenomenon that probably results (as previously indicated) from the reaction of urea with formaldehyde to form water-soluble monomethyol urea.[14] The overall reaction can be shown as follows:

$$(CH_2)_6N_4 \cdot HNO_3 + 3HNO_3 + 6H_2O + 6(NH_2)_2CO \rightleftarrows 4NH_4NO_3 + 6NH_2CONHCH_2OH \ .$$

The effect of urea on HMTA decomposition is described further in Sect. 3.5.

The $HMTA \cdot HNO_3$ will also decompose at elevated temperatures when urea is not present. When HMTA was titrated with HNO_3 at 68°C, a protonation-decomposition pH profile very similar to curve B in Fig. 6 was obtained. Titration of HMTA solutions containing urea with HNO_3 at elevated temperatures also gave this type of profile. Even at a temperature as high as 90°C, the protonation reaction proceeded essentially to completion before decomposition was noted. Although accurate values could not be obtained at the higher temperatures due to the evaporation of solution during titration, we can reasonably estimate that protonation proceeded to 90-95% completion prior to the onset of decomposition at nearly all conditions of interest.

This behavior is of particular interest in understanding uranium precipitation behavior because it indicates that most of the hydrogen ion generated by uranium hydrolysis is neutralized via the protonation reaction. At high HMTA/U mol ratios and low NO_3^*/U mol ratios, $HMTA \cdot HNO_3$ decomposition would not be expected to occur at all.

The percentage of the H^+ that would be expected to react via protonation (assuming that 95% of the HMTA is protonated prior to HMTA decomposition) as a function of HMTA/U and NO_3^*/U mol ratios and uranium concentration is given in Table 2. These data show that at low NO_3^*/U mol ratios (normally preferred for urania microsphere preparation), ~70 to 100% of the hydrogen ion reacts via the protonation reaction.

The rapid protonation of HMTA indicates that both protonation and hydrolysis occur during the initial pH decrease (see the pH profile,

Table 2. Percentage of available H^+ neutralized by HMTA protonation

	NO_3^*/U mol ratio					
	1.50	1.60	1.70	1.80	1.90	2.00
HMTA/U mol ratio	1.73	1.73	1.73	1.73	1.73	1.73
HMTA conc., M (95%)	1.50	1.50	1.50	1.50	1.50	1.50
H^+ conc., M[a,b]	1.37	1.46	1.55	1.64	1.73	1.82
% H^+ neutralized by protonation	100	100	97	91	87	82
HMTA/U mol ratio	1.51	1.51	1.51	1.51	1.51	1.51
HMTA conc., M (95%)	1.39	1.39	1.39	1.39	1.39	1.39
H^+ conc., M[a,c]	1.46	1.55	1.65	1.75	1.84	1.94
% H^+ neutralized by protonation	95	90	84	79	76	72
HMTA/U mol ratio	1.30	1.30	1.30	1.30	1.30	1.30
HMTA conc., M (95%)	1.28	1.28	1.28	1.28	1.28	1.28
H^+ conc., M[a,d]	1.56	1.66	1.77	1.87	1.98	2.08
% H^+ neutralized by protonation	82	77	72	68	65	62
HMTA/U mol ratio	1.10	1.10	1.10	1.10	1.10	1.10
HMTA conc., M (95%)	1.16	1.16	1.16	1.16	1.16	1.16
H^+ conc., M[a,e]	1.67	1.78	1.89	2.00	2.11	2.22
% H^+ neutralized by protonation	69	65	61	58	55	52

[a]The concentration of H^+ produced by complete uranyl hydrolysis is equal to the uranium concentration (M) times the NO_3^*/U mol ratio.
[b]Uranium concentration = 0.91 M.
[c]Uranium concentration = 0.97 M.
[d]Uranium concentration = 1.04 M.
[e]Uranium concentration = 1.11 M.

Fig. 5) when broths are heated, with the rate of decrease (which is temperature dependent) reflecting the difference in the two reaction rates. The subsequent increase in pH occurs when continued HMTA protonation and/or decomposition proceeds faster than the H^+ formation rate.

3.5 CHEMICAL ROLE OF UREA

Urea plays two significant roles during the precipitation and gelation of uranium: (1) it complexes the uranyl ions in the feed broth at 0°C, thus preventing premature precipitation; and (2) it accelerates $HMTA \cdot HNO_3$ decomposition at a given temperature by reacting with formaldehyde, which is a product of the decomposition.

In aqueous solutions at low temperatures, urea has been reported to complex with uranyl ions in a mol ratio of 2, as shown in the following equation:[10]

$$UO_2^{2+} + 2CO(NH_2)_2 \rightleftarrows UO_2[CO(NH_2)_2]_2^{2+} .$$

In previous studies, we found that a mol ratio of ~1.0 was adequate to provide a stable broth at 0°C. These studies were made with uranium-plutonium feeds (U/U+Pu mol ratio = 0.75); however, urea/metal mol ratios as low as 0.91 provided stable broths at 0°C for periods of 1 h or more.

Continuous pH profiles that demonstrate these effects of urea during uranium precipitation at 65°C are shown in Fig. 7. In the first experiment (curve A) where the urea/U mol ratio was >1, the feed broth was stable at 0°C and complete precipitation of the uranium was obtained as the broth was heated to 65°C, producing the pH profile shown. In the second experiment (curve B) where the urea/U mol ratio was decreased from 1.25 to 0.91, some uranium precipitation occurred at 0°C; however, when the broth was heated, the pH profile was not altered except for a slight decrease in pH and the uranium was totally precipitated. When no urea was present, as in the third experiment (curve C), however, the feed broth was not stable at 0°C and the $HMTA \cdot HNO_3$ decomposition that is required for complete uranium precipitation at these conditions was so slow that total precipitation did not occur in 20 min and the pH did not increase above

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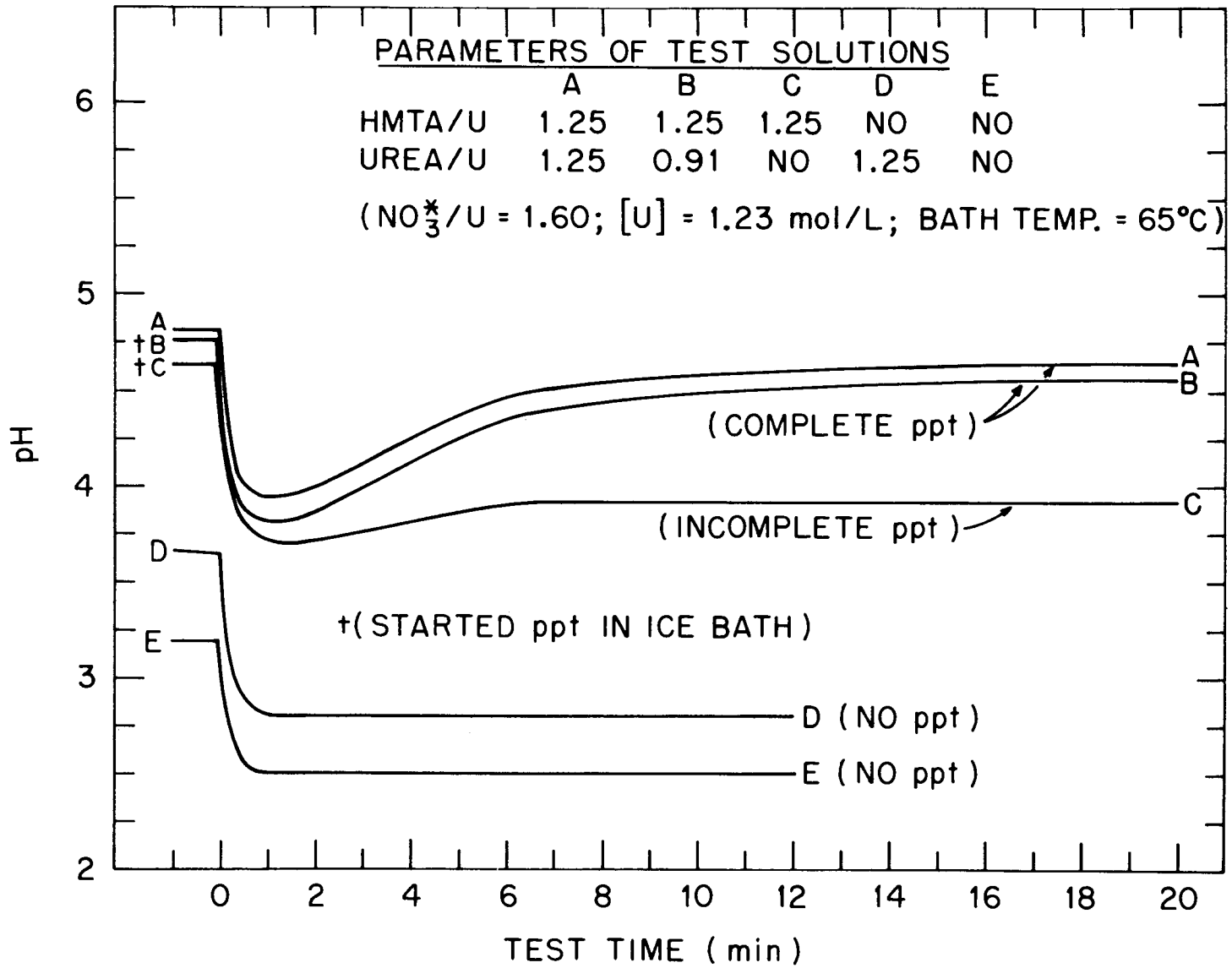

Fig. 7. Effect of urea/uranium mol ratios on pH-vs-time profiles.

~3.9. The small variations in the pH of the broths at 0°C in these three experiments reflect the contribution of urea to total broth pH. (In all three experiments, ~84% of the H^+ was neutralized by HMTA protonation.)

Curves D and E (Fig. 7) demonstrate the effect of heating ADUN with and without urea when HMTA is not present. The presence of urea (curve D) caused an increase in the broth pH because it is a weak base (log k = 0.1 at 25°C),[19] but did not otherwise affect ADUN hydrolysis. In each experiment, the pH decreased when the broth was heated as a result of uranium hydrolysis; however, precipitation did not occur because of the low equilibrium pH values (precipitation occurs at a pH >3.25).

The rate of decomposition of protonated HMTA in the presence of urea increases rapidly with increasing temperature. This relationship can be demonstrated by potentiometric titrations of HMTA-urea solutions such as those shown in Fig. 6. As previously mentioned in relation to curve B of Fig. 6, ~10 min was required for pH equilibrium to occur due to the very slow decomposition of $HMTA \cdot HNO_3$ at 25°C when additions of acid were made beyond the equivalence point. Although efforts were not made in this study to determine precise $HMTA \cdot HNO_3$ decomposition rates as a function of temperature, it was observed that pH equilibrium is achieved much more rapidly at 50°C and is virtually instantaneous at 90°C.

3.6 EFFECTS OF PROCESS VARIABLES ON REACTION KINETICS AND SYSTEM pH AS INDICATED BY CONTINUOUS pH PROFILES

The pH-time-temperature profiles obtained when feed broths at 0°C are heated provide useful information concerning the effect of process variables on the system pH. They also provide qualitative insight concerning the effects of process variables on reaction rates.

The principal variables studied were (1) the HMTA/U mol ratio, (2) the NO_3^*/U mol ratio, and (3) the reaction temperature. Uranium concentration, which is also a potentially significant variable, was not studied extensively because frequently it cannot be varied to a significant extent in a given process.

3.6.1 Effects of NO_3^*/U Mol Ratio as a Function of Temperature

The pH–time–temperature profiles for four feed broths that were heated to 70°C are presented in Fig. 8. These curves illustrate the variation in broth pH as a function of the NO_3^*/U mol ratio at a constant HMTA/U mol ratio of 1.30. The pH at which uranium precipitation was first detected (gelation induction time) is also shown. Precipitation generally occurred in the temperature range of >20 to <60°C, depending on the pH. Variation of the NO_3^*/U mol ratio from 1.50 to 2.00 resulted in a decrease in broth pH from 4.95 to 3.84 at 0°C and a corresponding pH minimum that decreased from ~4.10 to 3.10 as the solutions were heated. The final pH of each of the four solutions was within the range of 4.4 to 4.8 (after 10 min); at equilibrium, any differences in pH are likely due to small variations or differences in reagent concentrations.

Initial uranium precipitation was detectable in ~10 s at the lower nitrate ratios, whereas ~60 s was required at a NO_3^*/U mol ratio of 2.0. The longer gelation induction time was due to a low pH. Precipitation did not occur in these systems when the pH was lower than ~3.25.

The effects of temperature on pH profiles at NO_3^*/U mol ratios of 1.50, 1.60, 1.70, 1.80, and 2.00 are shown in Figs. 9, 10, 11, 12, and 13, respectively. These data demonstrate that the minimum pH obtained during gelation is a strong function of temperature at a given nitrate ratio and that both the temperature and the NO_3^*/U mol ratio (i.e., the initial degree of uranyl hydrolysis) affect the rate of pH change. At high temperatures (80 to 90°C) and low nitrate ratios (1.50 to 1.60) where the degree of hydrolysis was high, the minimum pH was obtained very rapidly and the pH approached the equilibrium value in ~1 min. At lower temperatures, however, significantly longer times were required to reach the pH minimum and the approach to the equilibrium pH was very slow (see Fig. 10).

The effect of temperature on the pH minimum was much less pronounced at higher NO_3^*/U mol ratios (1.70 to 2.00), as shown in Figs. 11 through 13. In addition, the minimum pH value and the time required to reach the minimum value showed less variation. At all nitrate ratios, however, the

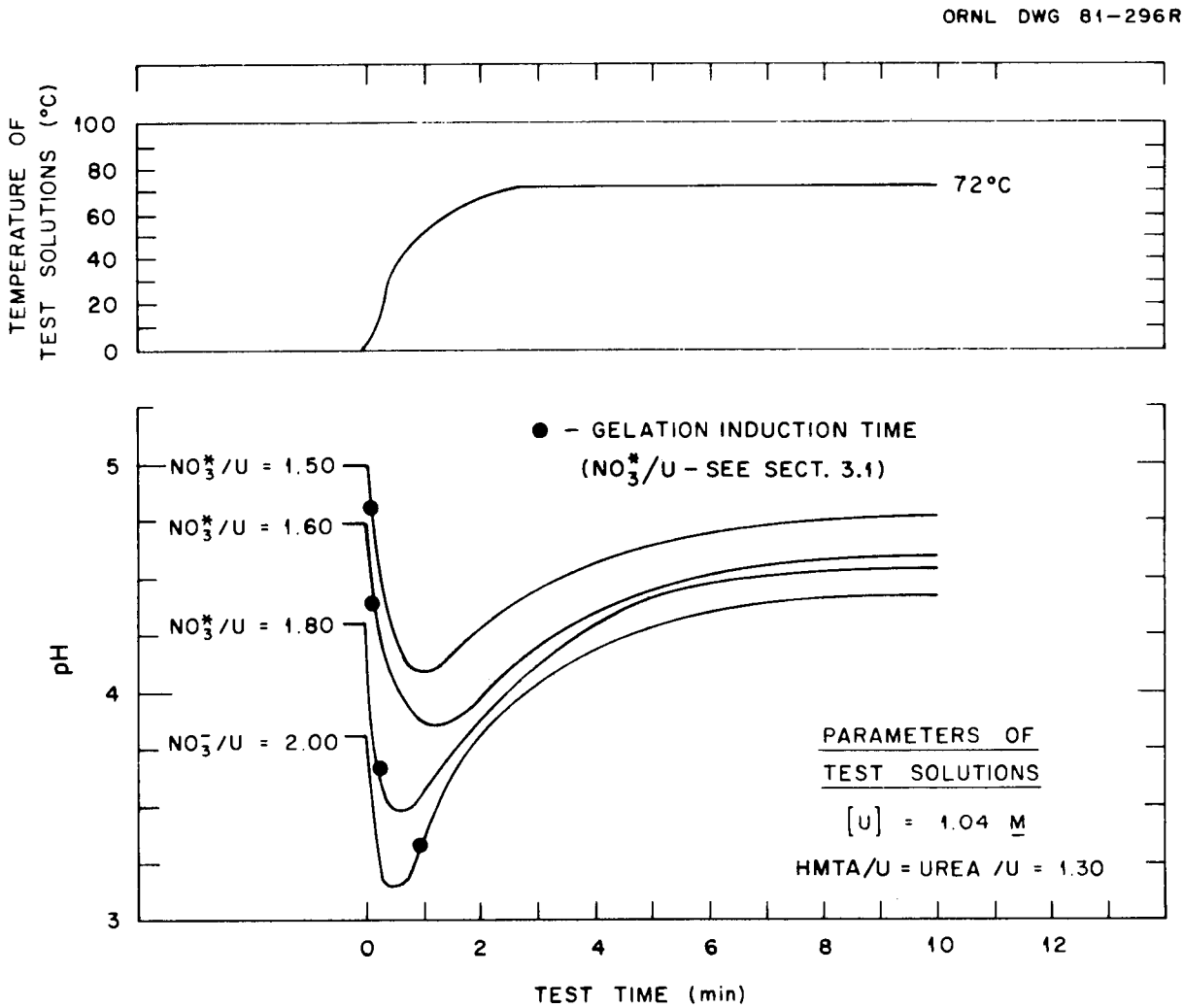

Fig. 8. Variations in pH-vs-time profiles at 72°C as a function of NO_3^*/U mol ratios.

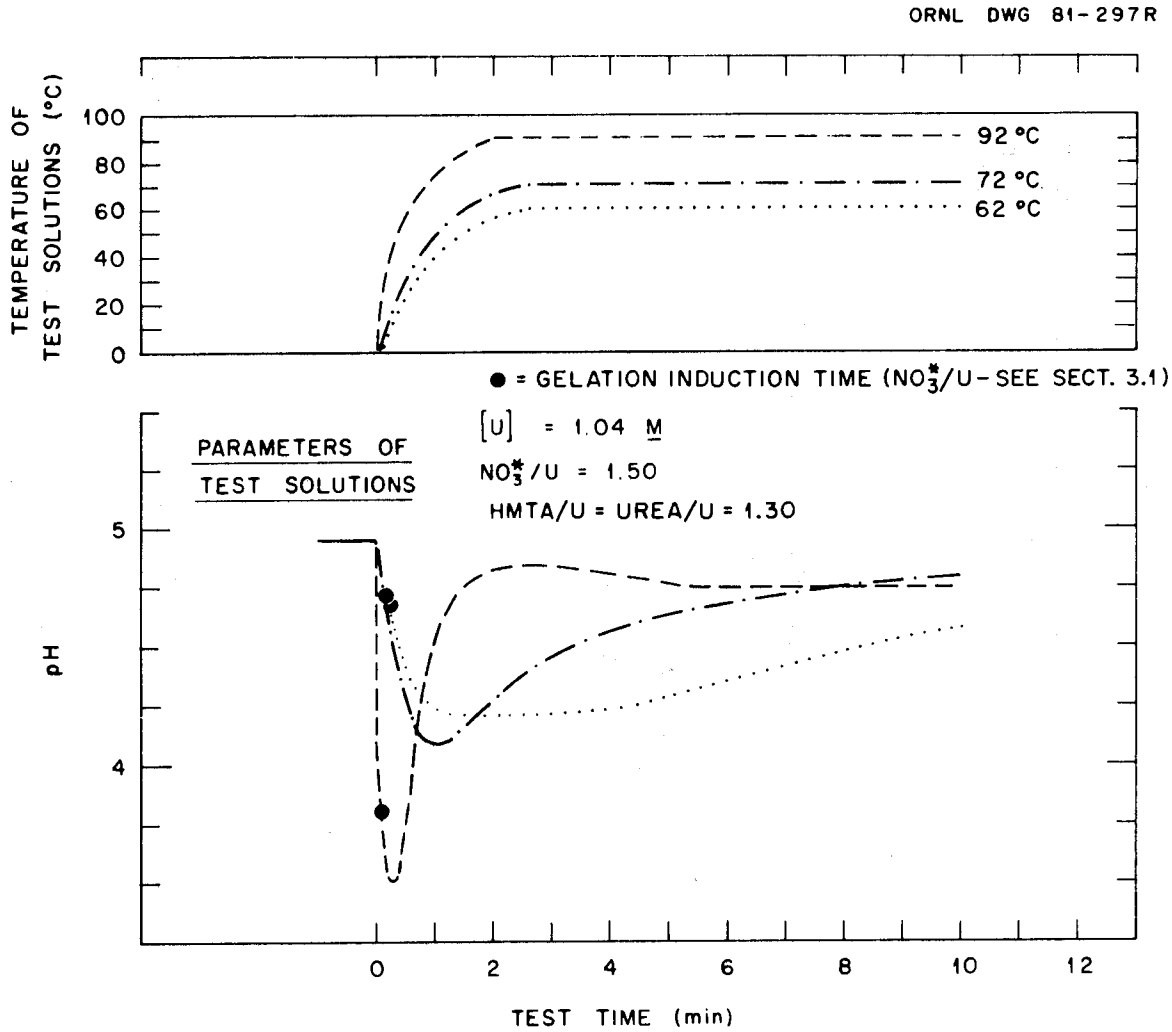

Fig. 9. Effect of temperature on pH-vs-time profiles. (Solution temperatures are shown for each corresponding pH profile.)

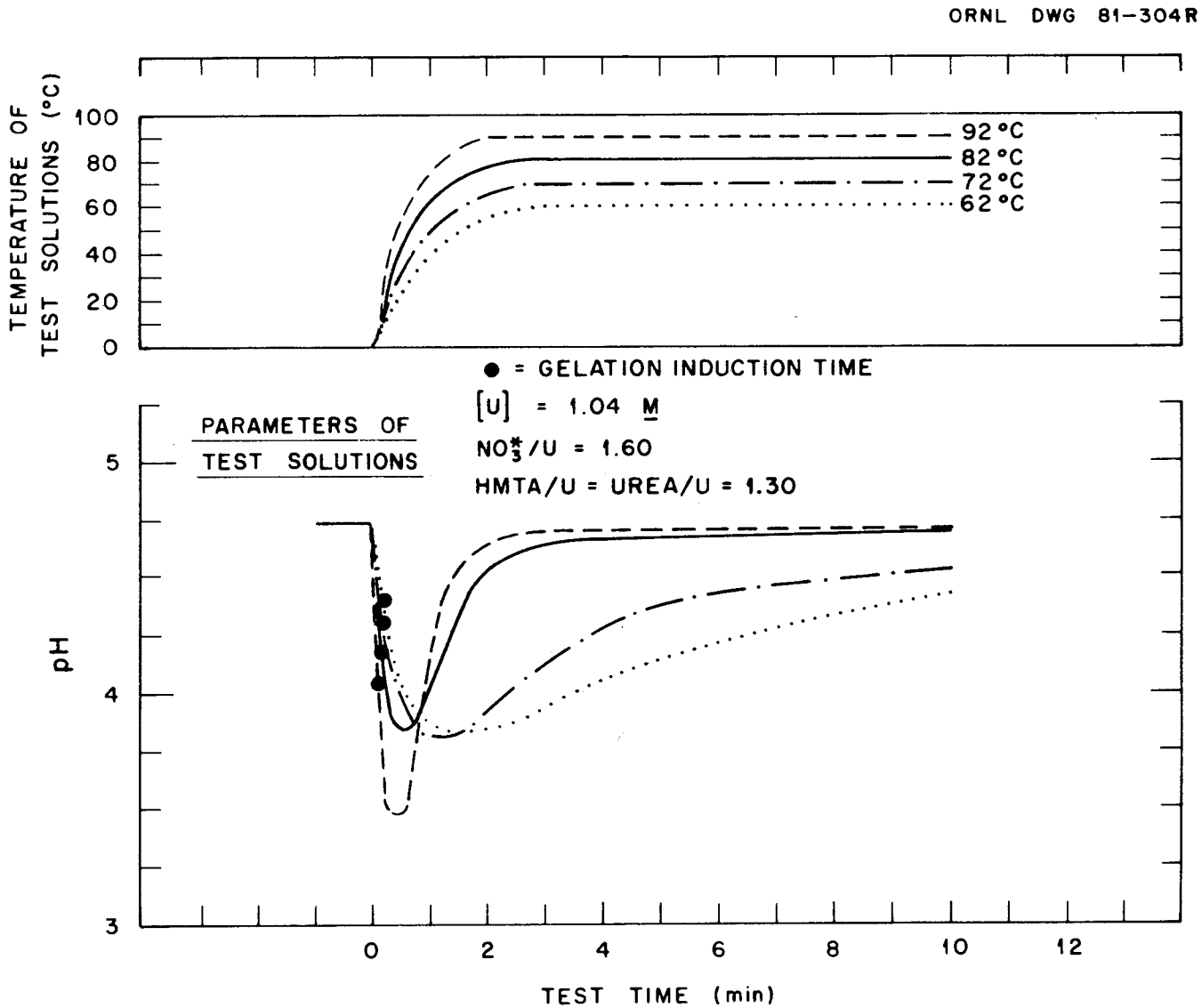

Fig. 10. Effect of temperature on pH–vs–time profiles. (Solution temperatures are shown for each corresponding pH profile.)

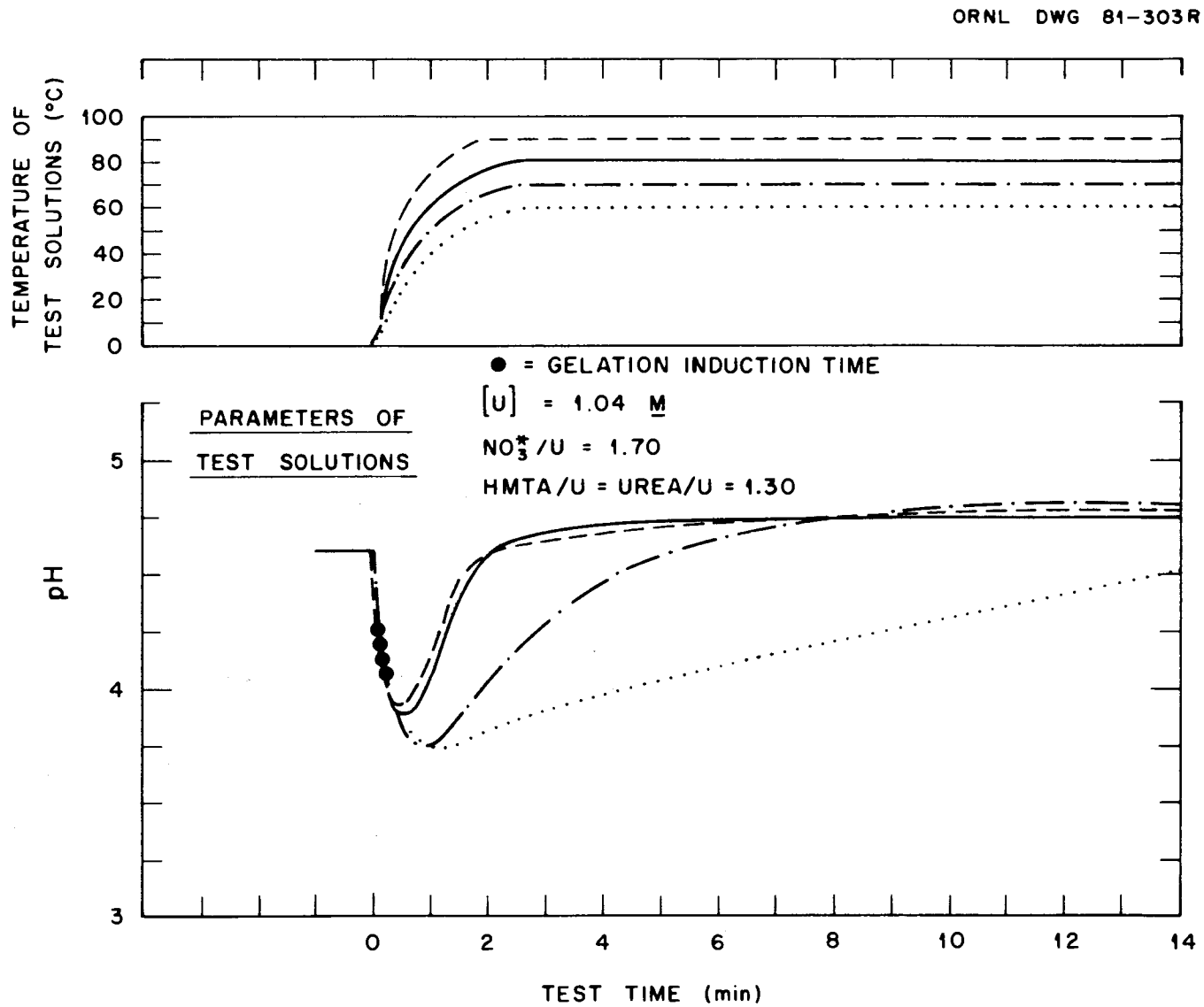

Fig. 11. Effect of temperature on pH-vs-time profiles. (Solution temperatures are shown for each corresponding pH profile.)

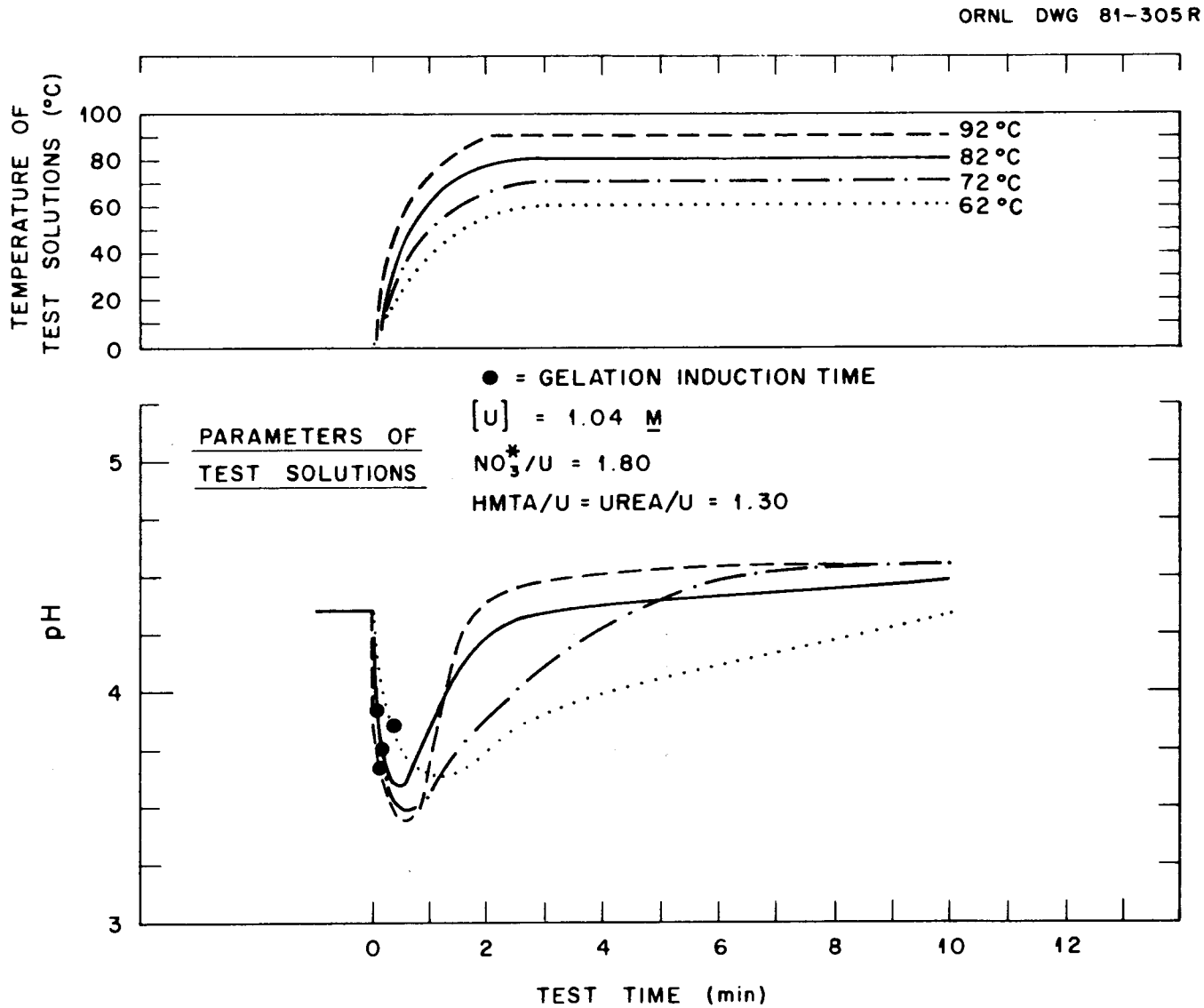

Fig. 12. Effect of temperature on pH-vs-time profiles. (Solution temperatures are shown for each corresponding pH profile.)

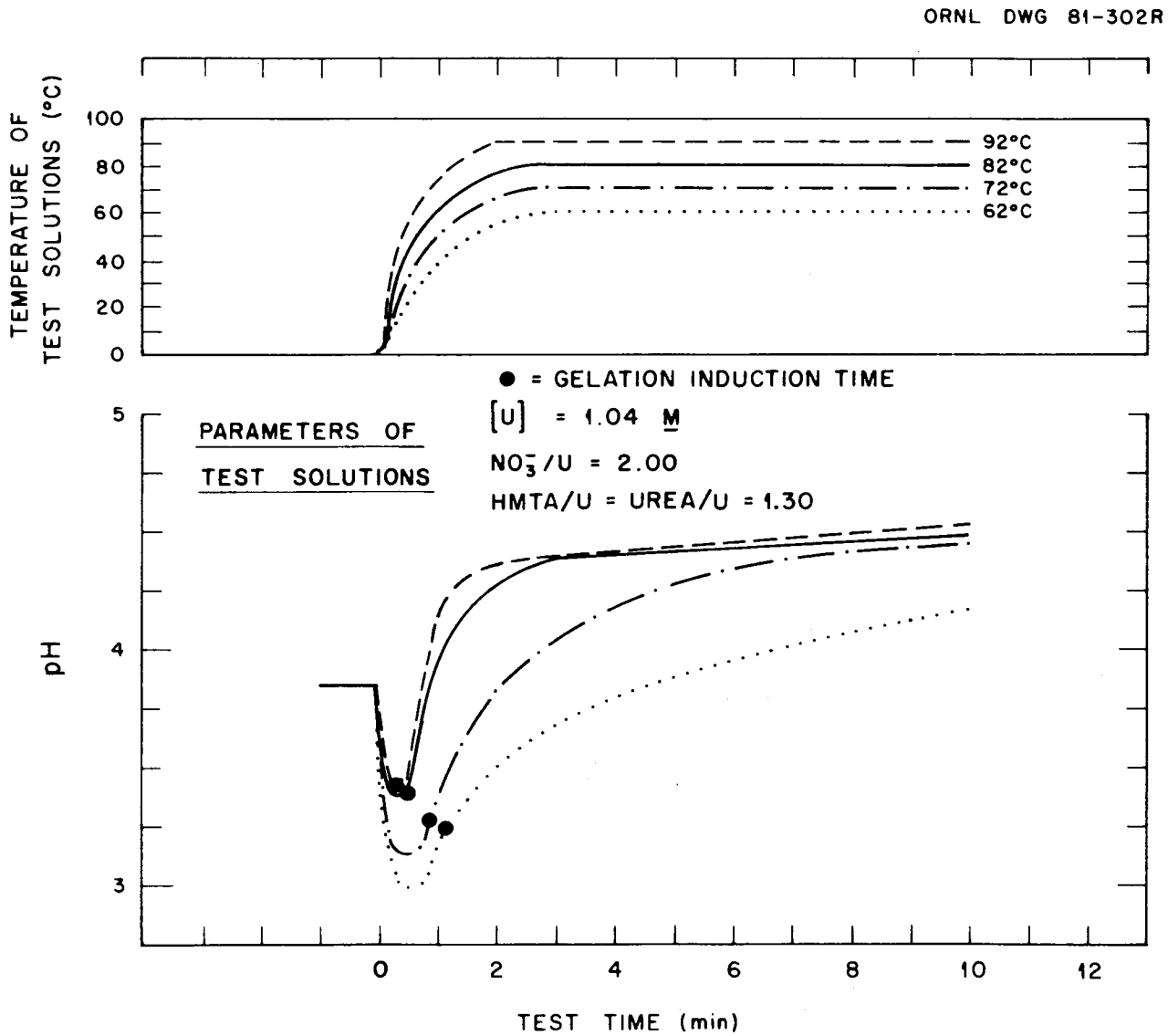

Fig. 13. Effect of temperature on pH-vs-time profiles. (Solution temperatures are shown for each corresponding pH profile.)

temperature strongly affected the time required for pH equilibrium. In fact, at 60°C, pH equilibrium was not obtained in 10 min at any NO_3^*/U ratio.

These effects have also been observed during actual microsphere preparation. Microsphere gelation time (i.e., the time required for a microsphere to gel as determined by visual observation) has been found to increase significantly with increasing NO_3^*/U mol ratio and with decreasing temperature.

3.6.2 Effects of HMTA/U Mol Ratio as a Function of Temperature

Based on a limited amount of data, we conclude that variations in the HMTA/U mol ratio do change the broth pH and the gelation pH range (Fig. 14); however, they do not appreciably alter the rate of pH change in the temperature range shown. In other words, reaction rates as indicated by the shapes of the profiles at 90°C are very comparable at HMTA/U ratios of 1.10, 1.30, and 1.73; only the minimum pH values appear to be changed. The same is true at 60°C for the three HMTA/U ratios. This factor is additionally shown in Fig. 15, where the rates of pH change are very similar at HMTA/U mol ratios of 1.00 to 1.60. Comparable data at higher NO_3^*/U mol ratios (>1.60)are not available.

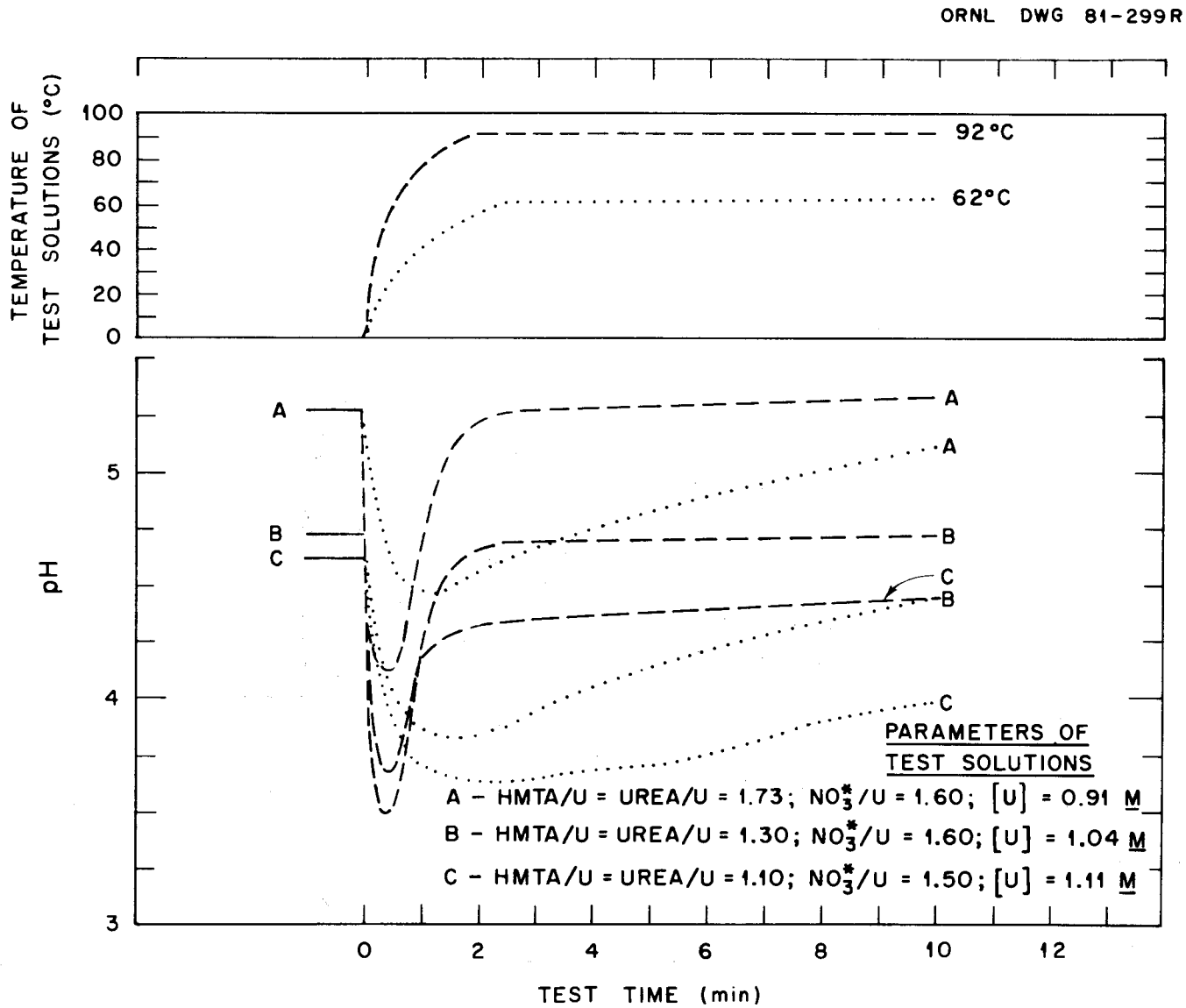

Fig. 14. Effect of HMTA/U mol ratios on pH–vs–time profiles as a function of temperature. (Solution temperatures are shown above for each temperature.)

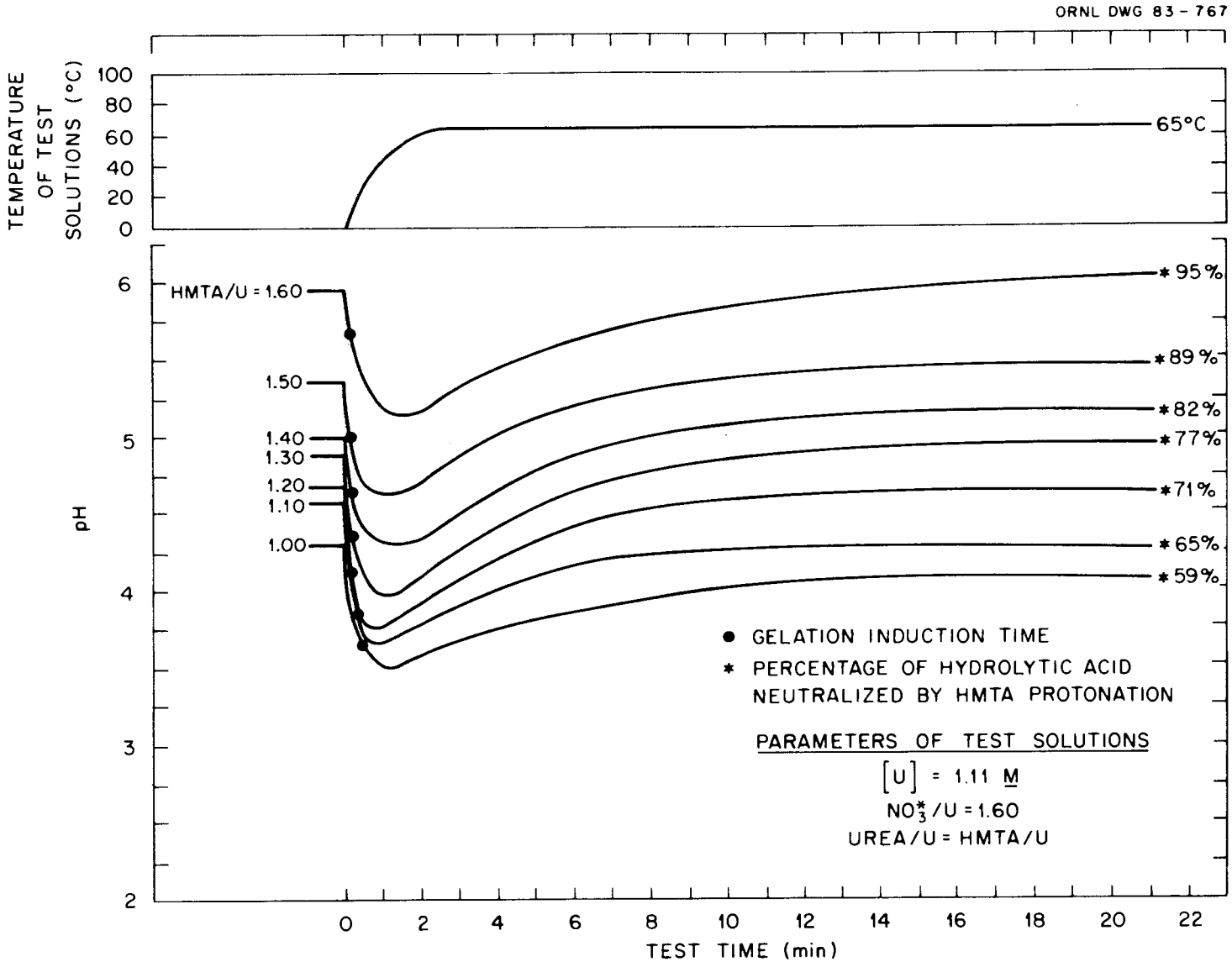

Fig. 15. Effect of varying the HMTA/U mol ratio on pH–vs–time profiles for broths heated to 65°C. (The percentage hydrolytic acid neutralized by HMTA protonation is also given.)

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