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Temperature Dependence of Henry's Law Constant for Hydrogen Cyanide. Generation of Trace Standard Gaseous Hydrogen Cyanide

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Abstract

Primary data for the temperature dependent solubility of HCN in water do not presently exist for low concentrations of HCN at environmentally or physiologically relevant temperatures. Henry's Law constant (K_H, M/atm) for the vapor-solution equilibrium of HCN was determined in 0.1 M sodium phosphate buffer (adjusted to pH 9.00±0.03 at 296.6±0.1 K) from 287–311 K. Stable gas phase concentrations of HCN are generated by established techniques, via air equilibration of aqueous cyanide partitioned by a microporous membrane. The effluent gaseous HCN, in equilibrium with the constant temperature aqueous cyanide, was collected in dilute NaOH and determined by a spectrophotometrically using cobinamide. The K_H of HCN may be expressed as $\ln K_H$ (M/atm) = (8205.7±341.9)/T − (25.323±1.144); r^2 = 0.9914) where T is the absolute temperature in K. This corresponds to 9.02 and 3.00 M/atm at 25 and 37.4 °C, respectively, compared to actual measurements of 9.86 and 3.22 at 25.0 and 37.8 °C, respectively. The technique also allows for convenient generation of trace levels of HCN at ppbv-ppmv levels that can be further diluted.

1. INTRODUCTION

Of many different inorganic and organic cyano compounds, hydrogen cyanide (HCN) is the simplest; HCN and its salts (NaCN, KCN, etc.) are well known for their high toxicity (1). Cyanide binds reversibly to the iron containing heme group of cytochrome a3 with resulting inhibition of mitochondrial electron chain transport, decreased energy formation and changes in the cellular redox state producing metabolic acidosis. Like O_2, HCN binds to heme Fe(II)

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Supporting Information Available
The Supporting Information includes an Excel file that illustrates aspects of calculations made and a pdf file that illustrates the cobinamide-cyanide reaction in water, and in phosphate and borate buffers, effect of sampling time and flow rate and constancy of calibration at different reaction times. These materials are available free of charge via the Internet at http://pubs.acs.org.

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in reduced cytochrome a3. However, in the presence of O_2 when the iron is oxidized to Fe(III), the binding increases markedly (2). The brain and heart are immediately and readily affected by cyanide (1). Paradoxically, low levels of cyanide are naturally found in biota (HCN at ppbv levels is readily detectable in human breath (3)). Industrial use of HCN and alkali cyanides are important: they are essential components in manufacturing synthetic fibers and plastics, agricultural herbicides, fumigants and insecticides, dyes and pigments, animal feed supplements, chelating agents for water treatment, plating and other specialty chemicals and pharmaceuticals, and in mining and processing gold (1,4). Thousands die annually from fire-associated smoke inhalation, HCN plays a major role in this (5,6). Of the physicochemical properties of HCN that governs its fate, transportation and uptake, its equilibrium aqueous solubility is very important.

Literature values of K_H for HCN vary considerably. Dzombak et al. (1) and WHO (7) cite diverse values from multiple sources. In Table 1, we provide a more comprehensive listing but many of these are secondary compilations with no clear indication of the primary data source. Vapor pressures of HCN solutions were listed first in 1928 (8). In the extant literature, the data are often extrapolated to other conditions/temperatures, some of the extrapolations likely are not justifiable (9). Temperatures and/or what concentration range the data actually apply to are often absent (10–11,13–15,18 20).

Table 2 summarizes available data on the temperature dependent K_H values of HCN. Dodge and Zabban's is the only work (21) that contains primary data at three different temperatures, the lowest being 64 °C, much higher than that relevant environmentally/physiologically. Moreover, if these data, obtained by dynamic stripping experiments where incomplete equilibration can occur, are extrapolated to 25 °C, the predicted K_H is an order of magnitude greater than most other reported values. Kotlik and Lebedeva (22) measured the HCN vapor pressure over 0.01– 0.5 M solutions of HCN at five different temperatures between 20–95 °C. They provide no primary data but a best fit equation (for conformity, we have converted all original equations to the M/atm units). Some books on HCN/cyanides cite this work (1,23) but by far the work most commonly cited is due to Edwards *et al.* In their first publication (24), Edwards *et al.* provided an equation valid over 10–70 °C (their original equation used aqueous concentration in molal units, in the domain of dilute aqueous solutions of our interest, this is not significantly different from molar (M) units). Subsequently they provided an alternate expression valid from 10–140 °C (25). These equations, especially the latter, have been widely cited and used by others in various forms (26,27), one corrected form is due to Yoo et al. (27–29). Ironically, as the source of primary data for the HCN-H_2O system, Edwards *et al.* (24,25) merely cite J. C. Siegle at Du Pont as personal communication. In short, the conditions of these experiments (saturation with pure HCN gas) are far removed from typical environmental conditions and/or the primary data are not accessible to the reader and/or the data are at odds with the bulk of other measurements.

Our interest in HCN stems from its role in smoke inhalation and its potential use by terrorists as a released toxic gas. In this paper, we have determined the K_H for HCN over a temperature range (287– 311 K) that spans the ambient to physiological range. We used a dynamic equilibrium system where equilibrium is established at the liquid-gas interface within a length of hydrophobic microporous tubing that is immersed in a cyanide bearing solution of known pH and ionic strength. Since its original introduction (30) this technique has been widely used for the evaluation of K_H and for generation of trace standard gas (31–39). A novel highly sensitive photometric assay for the measurement of HCN is also reported.

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2. EXPERIMENTAL SECTION

2.1 Reagents

All chemicals used were reagent grade or better and 18.2 MΩ·cm Milli-Q water (www.millipore.com) was used throughout. Pure cobinamide was produced by acid hydrolysis of cobalamin (www.sial.com) following Broderick *et al.* (40). The stock aqueous KCN solution was calibrated by a standard titrimetric method (41) and stored refrigerated.

2.2 Experimental Arrangements

Measurements were conducted using the arrangement previously reported (31–39). Briefly, ultra high purity grade cylinder N_2 was metered through a mass flow controller into a microporous polyvinylidene fluoride (PVDF) membrane tube (Enka, wall thickness 0.3 mm, i.d. 1.0 mm, length 50 cm, type R512) wholly immersed in the HCN generation solution contained in a 500 mL Erlenmeyer flask kept in a constant temperature bath (±0.1 °C). The generation solution consisted of 0.1 M Na_2HPO_4 solution (adjusted exactly to pH 9.00) to which various concentrations of KCN was added. With sufficient residence time of the flowing air in the porous PVDF tubing, the exit HCN is in chemical and thermal equilibrium with the generation solution. The generated HCN was collected by two serial 30-mL capacity fitted midget bubblers using 10 mL of 50 μM cobinamide in 60 mM NaOH as absorber. An aliquot from the bubbler contents was transferred to a 1 cm path length cuvette and the absorbance values at 580 and 700 nm were read with a photodiode array spectrophotometer (HP 8453, www.agilent.com). In initial experiments, the quantitative collection of cyanide by the upstream bubbler was verified by the lack of any perceptible absorbance change in the contents of the downstream bubbler. Henceforth, the absorbance of the downstream bubbler contents was measured only as a check and not for every sample.

pH was measured with a Φ71 pH meter (Beckman) by an Orion Ross combination electrode calibrated immediately before measurement by bracketing NIST-traceable pH 7 and 10 standard buffers. Buffer pH measurements were made at 23.5±0.1 °C, prior to cyanide addition. Solution manipulation after cyanide addition, including pH measurement, can cause loss of cyanide and thus overestimation of the total cyanide concentration in solution. But up to 0.76 mM KCN was added to the 100 mM Na_2HPO_4 buffer and this can affect the pH of the buffer, albeit slightly. We therefore measured the pH of the cyanide containing buffer not in the solution actually used for HCN generation but in an identically treated separate aliquot.

The effluent gas was collected for either 10 or 20 min, based on the anticipated p_{HCN}. The system was allowed to equilibrate for 20 h before any actual measurement was made. For any given combination of cyanide solution concentration and temperature, triplicate measurements were made.

CAUTION—Cyanide is extremely toxic and hazardous HCN is easily evolved. Care must be taken to avoid skin contact and inhalation/ingestion. The entire experimental setup was located in a well-ventilated hood. Exit HCN generated in our experiments was trapped in a bubbler containing alkaline hypochlorite (5% bleach solution containing added alkali) before disposal (42). Comparable measures should be taken if similar experiments are performed.

3. RESULTS AND DISCUSSION

3.1. Cobinamide based colorimetric assay for cyanide

For structures of cobalamins and cobinamide, see (43). Hydroxycobalamin binds cyanide with a relatively high affinity (it is used to treat smoke inhalation victims (44)). The colorimetric detection of cyanide by cyanocobalamin to form dicyanocobalamin was recently suggested

(45). However, with a detection limit of 0.6 mM in a purely aqueous medium, it has limited utility. Cobinamide is the penultimate precursor in the biosynthesis of cyanocobalamin. It binds cyanide with 10^{10} times greater affinity than cyanocobalamin and may be a better cyanide poisoning antidote (46,47). Cobinamide also undergoes a greater absorbance change than does any of the cobalamins and can thus be used for sensitive photometric measurement of cyanide, down to low μM levels.

Figure 1 shows the spectra of 50 μM cobinamide in 60 mM NaOH with 0–75 μM cyanide added. It will be observed that the bands at ~365 and 580 nm increase in absorbance upon cyanide addition while the band at ~340 nm and the pair of bands centred at ~520 nm decrease in absorbance with cyanide addition. Similar experiments were first conducted with the same concentration of cobinamide in water, in 0.1 M phosphate and borate buffer solution (each at pH 9.00). While results were similar, the final absorbance changed significantly with time (See Figure S1–S3 in the supporting information (SI) for details). While reproducible timing is not an issue in any automated procedure (e.g., flow-injection or similar procedure) where the collected cyanide is reacted with the reagent on-line, it is problematic in manual assays, especially when cobinamide is already in the absorber. We found that when cobinamide is made in an appropriate NaOH concentration, the product absorbance becomes stable after a short period (Figure 2). With 60 mM NaOH, after >~ 3 min, the response is reasonably stable (Figure 3); calibration slopes after reaction times >5 min are essentially invariant (detailed numerical data can be seen in Table S1 in SI). We will describe cobinamide-based cyanide determination in greater detail elsewhere. Presently, we measured three “unknown” samples, nominally 20.0, 40.0 and 60.0 μM in triplicate by the present method and by the Chloramine-T/pyridine-barbituric acid standard method (48), each calibrated independently. There was no statistical difference between the analytical results at the 95% confidence level by the one tailed *t*-test and the correlation coefficient between the two sets of analytical results was 0.9992. In addition, with the HCN generation and capture arrangement (50 μM cobinamide in 60 mM NaOH absorber), A_{580nm} increased linearly both with the sampling time (up to 20 min under these conditions, $r^2 = 0.9967$, after this the dicyano complex begins to form and the slope actually increases) and the flow rate (9–30 sccm, $r^2 = 0.9985$); details can be viewed in Figure S4 in Supporting Information. These data suggest that alkaline cobinamide can be reliably used for cyanide measurement. Of course, batch mode measurements cannot take advantage of the ultimate capabilities of such a method; we will describe sub-micromolar limits of detection in a flow system in a separate article in the near future.

3.2 The Henry’s Law Constant of HCN

A high HCN to CN^- ratio (as at a low pH) induces volatilization losses soon as the solution is made and this needs to be avoided. To maintain reasonable proximity to physiological pH, we have chosen a pH of 9 as a compromise. Of course, HCN is partially ionized at this pH and this fractional ionization, dependent on the temperature dependent dissociation constant of HCN, K_D, must be accurately ascertained. We have chosen to use K_D as given in (1):

$$K_D = 10^{-9.24} / \exp\left((\Delta H_{r,298}/R)^{*}(1/T - 1/298.15)\right) \quad (1)$$

where pK_D is 9.24 at 298.15 K, $\Delta H_{r,\,298}$ is the standard enthalpy of reaction at 298.15 K, 135.1 kJ/mol (49). The concentration of undissociated hydrogen cyanide in solution, [HCN] can now be computed from

$$[HCN] = [CN^-]_T (10^{-pH} \gamma_{CN-}) / (10^{-pH} \gamma_{CN-} + K_D) \quad (2)$$

Here pH and the activity of the cyanide ion, γ_{CN-}, are both temperature dependent quantities and require further considerations.

3.2.1. Buffer pH change upon cyanide addition and temperature correction—The pH of a 0.1 M pH 9.012 Na_2HPO_4 buffer increased in pH 0.006, 0.027, 0.047 and 0.079 pH units upon the incorporation of 0.2, 0.4, 0.6 and 0.8 mM cyanide. These data fit the exponential relationship (within these limits)

$$\Delta pH = 0.125\,(CN^-,\,mM)^{1.844} \tag{3}$$

With an r^2 of 0.9911. The delta pH values anticipated for the specific amounts of cyanide added to the generation solutions were obtained by interpolation with eqn. 3. Calibration buffers of pH 7 and 10 used here also specify pH values at 10–40 °C. We calibrated the pH meter at each generation temperature with these buffers, using the temperature specified pH values. The temperature equilibrated pH o the 0.1 M Na_2HPO_4 solution was measured at that specific temperature with the meter calibrated at that temperature. The difference in pH from that measured at 23.5 °C was sigmoidal in shape, the pH increased by ~0.2 pH units at the lowest temperature studied and decreased by 0.05 pH units by 35 °C this difference remaining constant up to 38 °C. The actual pH of the cyanide-bearing generation solution at any specific temperature was thus adjusted by this temperature induced change.

3.2.2. Activity coefficient of cyanide—Scatchard and Breckenridge (50) have measured the mean activity coefficient in 0.1 m Na_2HPO_4 solution to be 0.480 (see also Table 12-3-1 A, Harned and Owen (51)). At this concentration, the difference between molality and molarity is insignificant. From the literature values of K_a values for phosphoric acid (2.15, 7.20 and 12.38, respectively, ref. (52)), in iterative procedures (by initially assuming the ionic strength to be 0.3 M based on the formal concentration and using the Extended Debye-Hückel Equation (EDHE, see ref. (53)), we find that the self consistent ionic strength is 0.299 M; 98+% of the P-species remains the hydrogenphosphate dianion (ion size parameter (see ref. 53) for $H_2PO_4^-$ was assumed to be 4.5 A). For a solution of this ionic strength, the mean ionic activity coefficient in a 0.1 M Na_2HPO_4 solution by EDHE (we assume ion size parameter of 4 A for Na^+ and 4.5 A for $H_2PO_4^-$, resulting in a mean distance of closest approach to be 4.25 A) will be 0.482, remarkably close to the experimental measurement in (50). We can therefore use EDHE with confidence for the present purpose: we use this in the form:

$$-\log\gamma_{CN-} = \frac{1.83\times10^6(DT)^{-1.5}\sqrt{I}}{1+50.3(DT)^{-0.5}a\sqrt{I}} \tag{4}$$

Where γ_{CN-} is the activity coefficient of cyanide, D is the dielectric constant of water, T is the absolute temperature in K, I is the ionic strength and *a* is the mean distance of closest approach in angstroms. In the present case the last parameter pertains to the approach between Na^+ and CN^-. Given 3 A as the ion size parameter for CN^- and 4 A for Na^+ (53), we use a = 3.5 A. The reader interested in calculation details is referred to the Excel® spreadsheet in the supporting information. γ_{CN-} showed little dependence on temperature over this limited experimental range, remaining essentially constant at 0.673±0.003. In dilute solutions, the activity coefficient of unionized HCN (aq) may be regarded as unity.

3.2.3. Equilibrium data and comparison—At 6 different temperatures from 14.2 to 37.8 °C, we used three different total cyanide concentrations in the generation solution, 0.18–0.20, 0.38, and 0.57 mM. In addition, three additional concentrations, 0.015, 0.094 and 0.76 mM, were tested at 25 °C, the equilibrium gaseous HCN concentrations ranged from 700 ppbv to 40 ppmv; detailed results are presented in Figure 4.

Figure 5 shows the ln K_H values obtained in this work plotted against reciprocal absolute temperature and compared with the other data describing temperature dependence in the literature. It will be observed that at temperatures below 25 °C, the results from this work are quite close to the results given by the Edwards *et al*. expressions (24,25) while the Kotlik-Lebedeva equation (22) agrees with our value at 28.8 °C and over/under predicts our data at temperatures above/below this temperature. Yoo *et al*.'s (27) K_H expression runs 0.4 ln units higher than Edwards *et al*. (1978) and is thus also consistently above our data. Dodge and Zabban's data (21) show much higher K_H values than all others but it is remarkable that the slope of their data is remarkably close to ours. At 25 °C, our measured value is 9.86 and that predicted from our temperature dependent equation is 9.02. The values in Table 1 for which the temperature is explicitly 25 °C average to 9.82±2.09, this agreement is thus remarkably good.

At higher temperatures, especially as we approach physiological temperature at the high end of our experimental range, our data progressively produce lower K_H values relative to the other expressions, this deserves comment. One salient difference between our work and the previous temperature dependent data largely lie in the absolute concentration range involved. Dimerization of HCN have been invoked in diverse situations, from interstellar clouds (54) to prebiotic synthesis of purine precursors from aqueous HCN (55,56). If there is any such dimerization in solution, at higher aqueous HCN concentration, the effect will be greater on K_H and will shift K_H to higher values. If this is the case, it would also suggest that HCN dimerization is promoted at higher temperatures. It is interesting that all the other data in Figure 5 except that of Dodge and Zabban (21) were obtained under static conditions. If the equilibration between dimeric and monomeric aqueous HCN is not rapid on the stripping time scale, it will explain why Dodge and Zabban's data, also obtained under dynamic conditions, predicts a similar H as our results.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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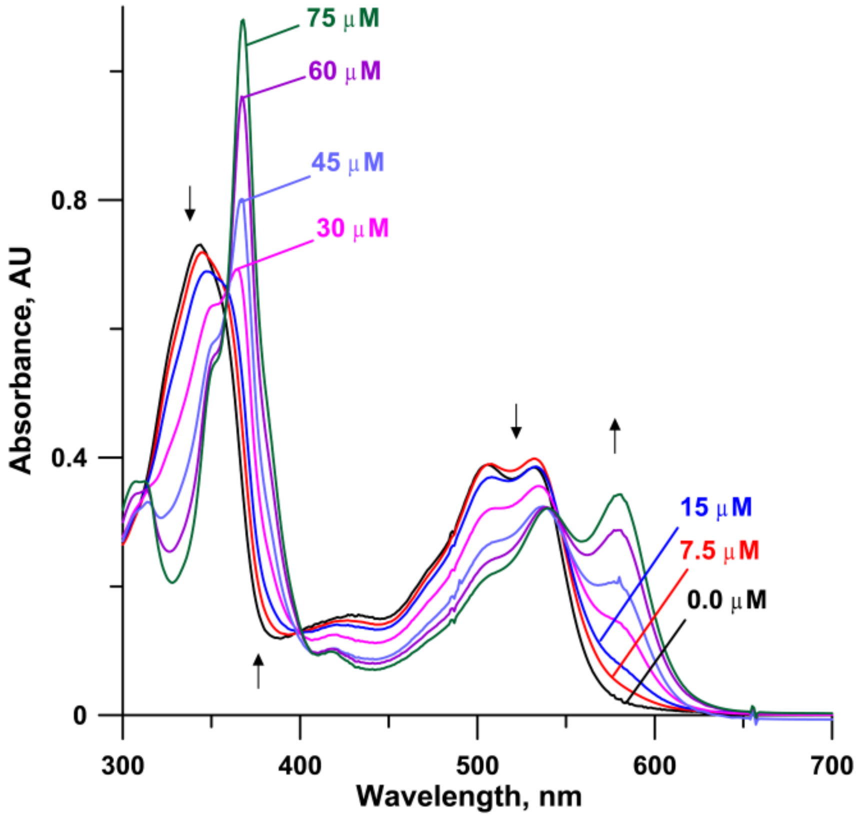

Figure 1.
Spectral change in 50 μM cobinamide prepared in 60 mM NaOH upon the addition of 0–75 μM cyanide. Spectra taken 10 min. after cyanide addition.

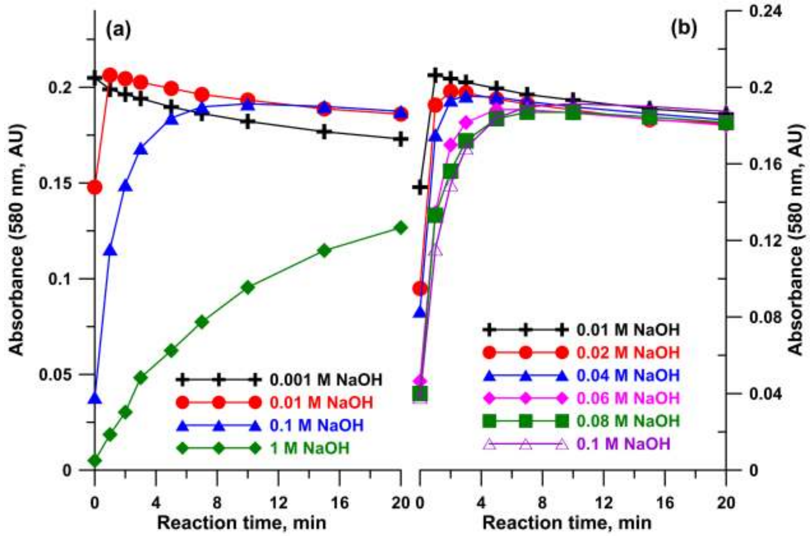

Figure 2.

Absorbance change at 580 nm at different reaction times (60 μM cyanide reacts with 50 μM cobinamide) (a) prepared in 0.001–1 M NaOH solution, (b) prepared in 0.01–0.1 M NaOH.

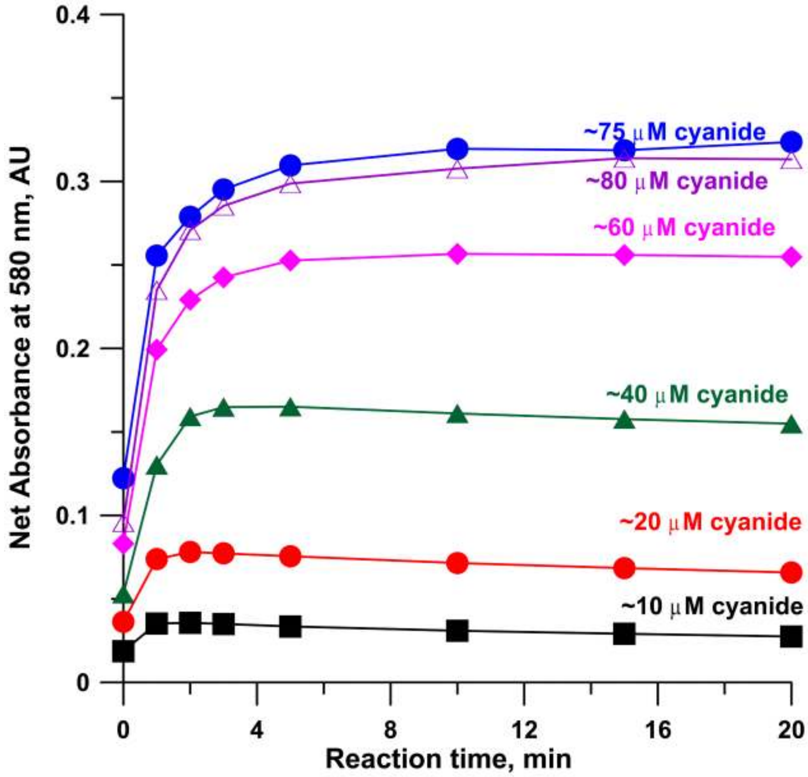

Figure 3.
Temporal change in absorbance at 580 nm after 10–75 M cyanide reacts with 50 μM cobinamide in 60 mM NaOH.

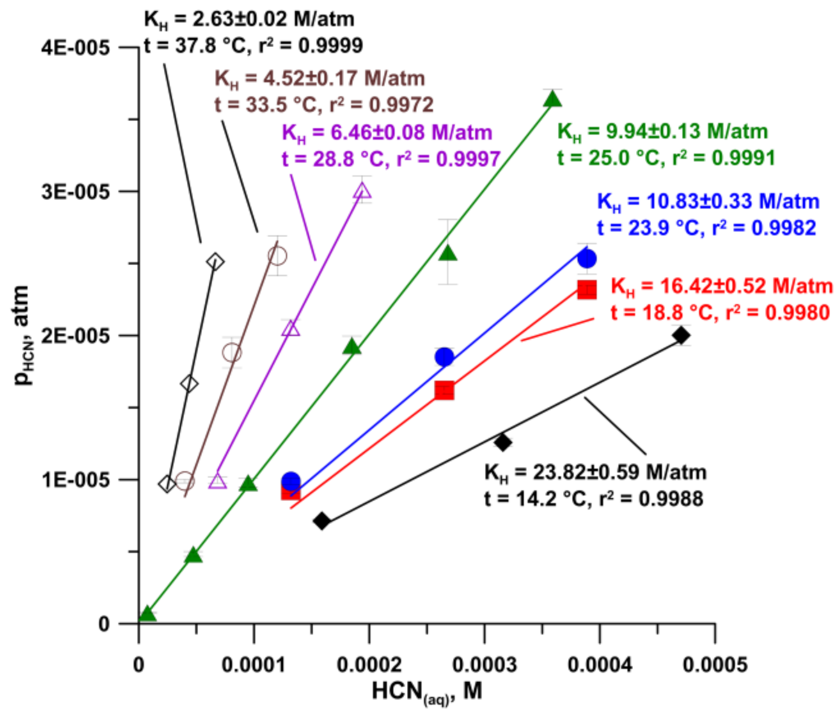

Figure 4.
Vapor pressures of HCN in equilibrium with 75 μM – 0.36 mM $HCN_{(aq)}$ at 7 different temperatures (n = 3 each).

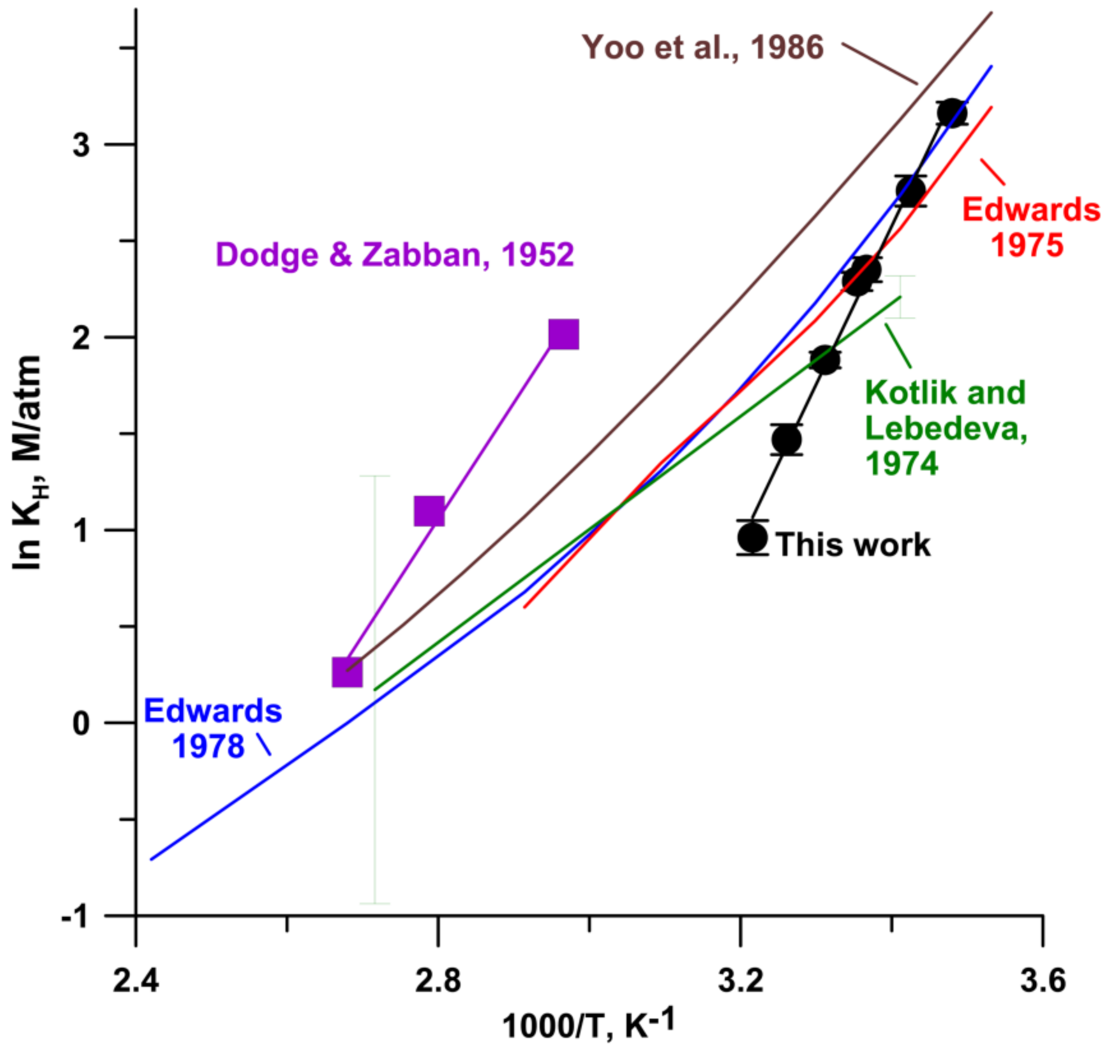

Figure 5.
The temperature dependent Henry's Law constant for HCN from this work compared to data (Dodge and Zabban, 1952) and equations in the literature. The error bars (n = 9–18 for each point in this work, n= 23 for the linear fit of Kotlik and Lebedeva) indicate ±1 standard deviation.

Table 1

Single temperature or unspecified temperature values for K_H for HCN

KH, M/atm	t, °C	pHCN, ppmv	Ref	Comments
13.3	18	138,000	8	Based on the lowest concentration data in this tabulation
9.3	25	197,000	9	Value extrapolated from above data
8.8–9.6	?	?	10	Secondary compilation, no sources are cited
7.5	?	?	11	Stated to be effective constant at pH 4, no sources cited
8.7	25	100	12	Value given in atm/mole fraction, extrapolated to infinite dilution
8.2–8.8	25	100	12,13	As for previous entry, data from (12), interpreted by authors of (13)
8.8	?	1500	13	As for previous entry, this paper has different values in a table than in text, tabulated values are given here; this result is for a pure cyanide solution
8.4–9.8	?	2190–4150	13	As for previous entry, results for a cyanide bearing synthetic leaching solution
10.5–11.6	?	2020–3030	13	As for previous entry, results for a cyanide based actual zinc leaching solution
13.7	?	?	1	Reference [1] cites this as from ref. [14], we were unable to locate this in ref. [14].
12	25	?	15	Secondary source, cites Edwards *et al.* (1978) that contains no primary data
12.2	20	2–40	16	Electronically published MS thesis
12.8	25	318–376	17	
9.4	?	?	18	Review, primary source not given
11.9	30	825	19	As interpreted in (16)
7.6	25	21	20	Static measurement of headspace by GC. Author suggests that static techniques produce lower K_H values

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Table 2

Temperature dependence of K_H values for HCN as reported in the literature

KH, M/atm	t, °C	pHCN, ppmv	Reference	Comments
7.5	64	19750	21	Most previous treatments assume that ref 21 has also measured results at 18 °C. In fact, these authors merely take that datum from the International critical tables (8). Based on their three experimental temperatures we derive the following linear eqn: ln KH (M/atm) = (6023.6±682.9)/T −15.817±1.922, r^2 = 0.9873
3.0	85.5	49380	21	r^2 drops to 0.8362 if a KH value of 13.3 at 18 C is added to these three points.
1.3	100	113960	21	
80.3	25	projected	21	25 °C computed from above equation for comparison, it is very far out of line from others. The computed value at 18 °C is 131, order of magnitude greater than the value of 13.3 obtained from (8).
See Eqn in Comments	20–95	8400–64600	22	Best fit eqn.: ln KH (M/atm) = (2931.0/T − 7.7897)±0.11; primary data not given, t= 20–95°C range was studied for C = 0.01–0.50 M. To estimate range of gas concn, we conservatively assume 0.50 M at 20°C and 0.01 M at 95°C.
7.7	25	not known, estimated ~10000+ ppm	22	25°C value computed for comparison, based on the above equation.
See Eqn in Comments	10–70	unknown, likely very high	24	ln KH (M/atm)= 212343/T − 7605.09 +1319.22*ln T − 2.08347*T valid over 10–70 °C, No primary source data which is cited as personal communication.
10.1	25	unknown	24	25°C value computed for comparison, based on the above eqn.
See Eqn in Comments	10–140	unknown, likely very high	25	ln KH (M/atm) = 49068.8/T − 1446.005 + 241.82*ln T − 0.315014*T valid over 10–140 °C, No primary source data: cited as personal communication. Used by many in various forms, see, e.g., (26)
11.6	25	unknown	25	25°C value computed for comparison, based on the above eqn.
See Eqn in Comments	0–100	See Comments	27	Says that it uses (25) and (28) as data source, when in fact (25) contains no primary data and (28) describes the dissociation constant of the ammonium ion. Cited as the sole source of KH by some authoritative compilations, e.g., ATSDR (29). Eqn given: ln KH (M/atm) = 6302.0/T −9.5850 − 3.1704*ln T + 0.03147*T
17.8	25	See Comments	27	25°C value computed for comparison based on the above equation.
See Eqn in Comments	14–38	0.8–36	This work	ln K_H (M/atm) = (8205.7±341.9)/T− (25.323±1.144), r^2 =0.9914, 24 measurement conditions each in triplicate, the value computed for 25 °C is 9.02
9.86	25	0.8–36	This work	This mean experimental value is within 10% of the value calculated from the temperature dependence equation.