1.) For field determinations, some of the characteristics are:
- low mass, low power, fast, and sensitive.

IMS is appropriate in some ways in that it is fast,
- i.e. separations occur on a time scale of ~30 msec, or so.
It also can operate with flow of air at atmosphere
- pressure, so compressed gases are not necessary, nor are
- fast pumping systems. It could be fairly low mass,
- and handheld commercial systems do exist. The ion
- source and vacuum system requirements help make it low
- power, i.e. use of $^{63}$Ni and operation at atm. pressure. Limits of
detection have been reported as low as 0.1 ppb. Alternative
approaches - GC/MS is too slow, and there can be problems with
- "sticky" analyte handling. MS/MS instruments can be bulky,
high power and mass instruments or the smaller versions can be
- low sensitivity. (Note that very large instruments can be "portable")
- "Portable" is a word with uncertain meaning,
- with respect to size.

2.) Drift times are inversely proportional to the
- ion mobility, $\mu$.

$$ \frac{1}{\mu} \propto \frac{m}{q} \cdot \frac{1}{R} \cdot \frac{1}{\text{collision cross section}} $$

The size, shape, and polarizability of the ion,
- For large ions, $\mu \propto \frac{8}{R}$

Note that the question is not about drift times,
- but about separation.
3) Here is a design that works:

Drift length might be 10-20 cm.
Electric field is on order of 300 V/cm

So this instrument could separate and detect Sami in air. However, it is important to note that this is a relatively low resolution separation instrument. At low concentrations in air, many other species may have the same CRSS section, and complete separation may be difficult. Therefore, selective ionization and/or MS detection may be necessary.

Note: you don't do ESI with a gas phase sample!

4.) $T_d = \frac{L^2}{V} = \frac{L}{K}$ at STP (as in this problem)

$K = K_0 = 1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

$V = 300 \text{ V/cm} \times 15 \text{ cm} = 4500 \text{ V}$
$L = 15 \text{ cm}^2$

$T_d = \frac{(15 \text{ cm})^2}{1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \times 4500 \text{ V}} = 0.033 \text{ s} = 33 \text{ msec}$

6 pts if right 50 ms
5) For all of IMS, chromatography, and M.S. we can
consider the resolving power as the maximum number
of separable species.
So, for IMS we can define resolving power as:
\[ \frac{\lambda}{\text{peak width at half-height}} \]
This number is on the order of 50 for state-of-the-art
benchtop IMS instruments.

For capillary gas chromatography, which could be used for
Serin-like species, the value for the corresponding
quantity, \( \frac{T_1}{(FWHM)} \), is 600 (3sec half-width, 30 min tR),
or \( \approx 10 \) times better than IMS (but much slower!)

For mass spectrometry, a reasonably achievable value for
a portable mass spectrometer might be \( \frac{M}{\Delta m} = 500 \) again.
(at least 10 times better, by this measure, M.S. is
des fast! So, IMS is a comparatively low resolutio
resolution separation technique, at this point.

6) There are two obvious ways:

1) Combine IMS with a complementary separation technique, like time-of-flight M.S., which could provide at a minimum M.W. 176.

2) Perform selective ionization.

For example, if you choose a negative CI reagent with an electron affinity just below
that of Serin, many interfering species may
not be ionized.

Note the problem specified (Field detection of Serin in air).
6.) continued
For full credit you must comment on the impact on the ease of use in a field environment. Combining with time-of-flight substantially adds to size and power, because of pumping, flight path and power components. On the other hand selective ionization could be conducted with little impact on size and power. Other methods include: adding drift gas detectors.

7.) Compared to Chromatography, IMS has the 12pts advantage that there is very little handling of the analyte, or in other words, little contact with surfaces. Many labile analytes, or thermally unstable analytes, or species like 

"tions are easy separated by Chromatography. IMS can be applied to any in mideable species. IMS separations are also much faster than Chromatographic separations, and do not require availability of the mobile phase. IMS can also separate isomers. But it is lower resolution compared to mass spectrometry, a main advantage Compared to mass spectrometry, a main advantage is that large and power hungry pumping systems are not required. And, again, isobaric species can be separated by IMS. Otherwise, IMS is fast, comparable sensitive, and you can do multiple separation stages in one instrument. These factors make it difficult for IMS to compete with mass spectrometry.
8.) Perhaps foremost, it can operate at atmospheric pressure, so the interface can be much simpler. It separates on a basis that is quite different from chromatography, but this does not make it unique, relative to mass spectrometry. Unlike M.S., IMS can separate isomers. Otherwise, resolution is poorer, dynamic range is poorer, and you can now do M.S/IMS with relatively small instruments. IMS is likely to be smaller and more rugged. The disadvantages are - poorer resolution, and it is not nearly as specific in information content as mass spectrometry.

9.) This is an easy one, but extremely important! The key word is “quantitative”. Instruments in general are not quantitative or not-quantitative. That's up to the scientist. For quantitative measurements of Sarin in air, you need a gas-phase standard of Sarin in air along with all the other components that might interfere. This is always hard to do! In this case, handling the material is tricky. Furthermore, it is likely to be adsorptive. Measurement scientists frequently ignore the likelihood of losses of the analyte in the intake lines. So, calibration with a gas-phase standard exactly as the instrument would be used in the field is essential!
Answer Key
Inorganic Chemistry Cumulative Exam
Purdue University
January 10, 2004

Today’s Topics: Winter Inorganic Chemistry and Bioinorganic Chemistry

Question 1:
A couple explanations have been proposed to explain the rust accelerating properties of salt. In one, rusting changes iron from the zero oxidation state to Fe$^{2+}$ or Fe$^{3+}$. These ions then take on oxide become iron oxide rust (e.g., Fe$_2$O$_3$). Electrons must move from the iron to the electron acceptor. One theory states that this movement of electrons away from the iron occurs faster in salty water. This salty water conducts more electrons, thereby promoting oxidation of iron.

Perhaps a more reasonable explanation can be found by looking at heats of formation. Iron metal is at 0 kcal/mole. Iron oxides such as Fe$_2$O$_3$ is at -195 kcal/mole and Fe$_3$O$_4$ is at -265 kcal/mole. Intermediate between iron metal and these states of rust is FeCl$_3$ at -95 kcal/mole. So the chloride from road salt may begin the thermodynamic decent from iron metal, thereby promoting rust formation. The chloride can take Fe metal to FeCl$_3$. Once the iron is out of the metallic state, rusting to the oxide is relatively quick. After FeCl$_3$ is transformed to the oxides, chloride is release and can begun the process again. Thus the chloride promotes rusting in a catalytic manner.

Question 2:
Orange juice contains citric acid and milk contains lactic acid. Taken from the Cold-Eeze web site: “The zinc gluconate glycine compound in COLD-EEZE® releases 93% of its ionic zinc (Zn$^{2+}$) into the mucosal membranes in the mouth. This is substantially more free zinc than released by zinc complexes with citrate, mannitol/sorbitol, tartrate, acetate or citric acid. The zinc ions readily bind to the (cold-causing) human rhinovirus (HRV) which prevents the virus from binding to somatic cells through intercellular adhesion molecules (ICAM), the “docking point” for HRV on the surface of nasal epithelial cells – subsequently reducing HRV duplication and further infection.” So if you take the lozenges with Zn$^{2+}$, but then drink milk or OJ, you will bind the Zn$^{2+}$ and not allow it to help your cold.

Question 3:
The design principles that might work best are using the chelate effect, hard-soft acid-base theory, and charge neutralization. So your ligand might be best to have multiple binding moieties, soft donors for the Cd$^{2+}$ such as S, P, or Se, and an overall charge of 2-. Many possibilities exist.

Question 4:
Similar to Question 3, but have a 3- ligand and hard donors for the Fe$^{3+}$ such as O and N.

Question 5:
Some examples: TiCp$_2$Cl$_2$ cancer drug, Gd(DOTA) MRI imaging agent, and Au(PEt$_3$)(thioglucose tetraacetate) for arthritis.
2. Comparing Eq. (4) with the generic equation \( aA + bB \to cC + dD \) gives the following results, valid for the reaction of Eq. (4), for the quantities in Eqs. (31) and (32):

\[
a = b = c = d = 1 \quad \text{(A.1)}
\]

\[
Q_e^0(T) = Q_{ii}^0(T), \quad Q_d^0(T) = Q_{oc}^0(T) \quad \text{(A.2)}
\]

\[
Q_e^0(T) = Q_{ii}^0(T), \quad Q_0^0(T) = Q_{bc}^0(T) \quad \text{(A.3)}
\]

\[
\Delta E^0 = -N_A \left[ E_{ii,0} + E_{oc,0} - E_{ii,0} - E_{bc,0} \right] \quad \text{(A.4a)}
\]

Using the corrections for the \( D_0 \)'s of atoms (H and D), given above Eq. (31), Eq. (A.4a) becomes

\[
\Delta E^0 = -N_A \left[ E_{ii,0} - E_{oc,0} - E_{ii,0} - E_{bc,0} \right] \quad \text{(A.4b)}
\]

where \( E_{ii,0} \) are the ground state energies of \( \text{H} \text{(D)}. \)

Using Eqs. (A.1) - (A.3) in Eq. (2) gives Eq. (6). Also, Eq. (A.4b) in Eq. (7).

b. From Eq. (2), the \( Q_j^0(T)'s \) in Eq. (6) may be written as

\[
Q_j^0(T) = Q^{tr}(T,V^q) Q^{rot}(T) Q^{vib}(T), \quad \text{for} \ \text{HCl and DCl} \quad \text{(A.5a)}
\]

and

\[
Q_j^0(T) = Q^{tr}(T,V^q), \quad \text{for} \ \text{H and D} \quad \text{(A.5b)}
\]
When we have used \( g_e \) = degeneracy of electronic ground state = 1 for \( ^2 \text{D} \), \( ^2 \text{Q} \) and \( ^2 \text{I} \) and = 2 for \( ^2 \text{S} \) and \( ^2 \text{P} \). (Thus \( g_e \) is equal from N and D in Eq. (1))

Using Eqs. (A.5) and (16) gives

\[
K_{eq} (T) = \left[ \frac{Q^{tr} (T, V) Q^{tr} \left( T, V \right)}{\frac{Q^{tr} \left( T, V \right)}{Q^{tr} (T, V)}} \right] \left[ \frac{Q^{rot} \left( T \right)}{Q^{rot} \left( T \right)} \right] \left[ \frac{Q^{vib} \left( T \right)}{Q^{vib} \left( T \right)} \right] \exp \left[ \frac{-\Delta E^o}{RT} \right]
\]

(A.6)

However for Eq. (13)

\[
Q^{tr} \left( T, V \right) = \left[ \frac{2 \pi m \hbar}{\hbar^2} \right] ^{3/2} V^3 \}
\]

(A.7a)

\[
Q^{rot} \left( T \right) = \frac{T}{\Theta^{rot}} = \left[ \frac{\pi^2 h^2 \Theta^{rot}}{\hbar} \right] M
\]

(A.7b)

\[
Q^{vib} \left( T \right) = \left[ 1 - 2 \Theta^{vib} \left( \Theta^{vib} \left( T \right) \right) \right] ^{-1}
\]

(A.7c)

Since \( \Theta \) is the same for both isotopes of HCl by the Born-Oppenheimer approximation, Eqs. (A.6) and (A.7) give

\[
K_{eq} (T) = \left( \frac{M_N M_{D_{Cl_1}, O}}{M_N M_{D_{Cl_1}, O}} \right) ^{3/2} \left( \frac{M_{D_{Cl_1}, O}}{M_{D_{Cl_1}, O}} \right) \left[ \frac{1 - \exp \left( -\Theta^{vib} \left( T \right) \right)}{1 - \exp \left( -\Theta^{rot} \left( T \right) \right)} \right] \exp \left[ \frac{-\Delta E^o}{RT} \right]
\]

(A.8)

Eq. (A.8) is the same as the result to be proven Eq. (8).

C. First consider \( \Delta E^o \) of Eq. (A.4b). For the H and D atoms the ground state energies \( E_{1D, 0} \) are nearly identical since the reduced mass

\[
E \to \text{H atoms and equal to the mass of an electron. Thus Eq. (A.4b) simplifies to}
\]

\[
\Delta E^o = -N_A \left[ E_{D_{Cl_1}, 0} - E_{D_{Cl_1}, 0} \right]
\]

(A.9)
Also for a diatomic molecule

$$D_0 = D_e - \frac{1}{2} \hbar \omega \omega_e$$  \hspace{1cm} (A.10)

where $D_0$ would be the dissociation energy if the molecule had no vibrational ground state. $D_e$ is the zero-point vibrational energy (classical dissociation energy) and $\omega_e = \frac{1}{2} \hbar \omega$ is the energy of the first excited vibrational level. The Born–Oppenheimer approximation is isotope independent. Hence, combining Eqs (A.9) and (A.10) gives

$$\Delta E^0 = N_A \frac{\hbar c}{\alpha} [\omega_e, D_e - \omega_e, \omega_e].$$ \hspace{1cm} (A.11)

Also from p. 23

$$\mathcal{H}^{\text{vib}} = \frac{\hbar c}{\alpha} \omega_e = \left( \frac{\hbar c}{\alpha} \right) \left( \frac{1}{3 \alpha c} \right) \left[ U''(r) \right]^{1/2}.$$ \hspace{1cm} (A.12)

Since $U''(r_e)$ is the same for both isotopes of HCl by the Born–Oppenheimer approximation, we have from Eq. (A.12) that

$$\frac{\mathcal{H}^{\text{vib}}_{\text{HCl}}}{\mathcal{H}^{\text{vib}}_{\text{HCl}^*}} = \frac{\omega_{e, \text{HCl}^*}}{\omega_{e, \text{HCl}}} = \left( \frac{M_{\text{HCl}^*}}{M_{\text{HCl}}} \right)^{1/2}.$$ \hspace{1cm} (A.13)

Eq. (A.13) permits elimination of $\mathcal{H}^{\text{vib}}_{\text{HCl}^*}$ and $\omega_{e, \text{HCl}^*}$ from Eqs. (A.8) and (A.11). Namely, Eq. (A.8) becomes

$$\Delta E^0 = N_A \frac{\hbar c}{\alpha} [\omega_e, D_e - \omega_e, \omega_e].$$
\[ K_{eq}(T) = \left( \frac{N_H N_{H_2}}{M_{H} M_{H_2}} \right)^{3/2} \left( \frac{N_{H_2}}{N_{H_2}} \right)^{\frac{1}{2}} \frac{\left[ 1 - 2 \exp \left( - \frac{\Theta_{H_2}}{T} \right) \right]}{1 - \exp \left( - \frac{\Theta_{H_2}}{T} \right)} \exp \left[ - \frac{\Delta E^0}{R T} \right] \] (A.14)

Also, Eq. (A.11) becomes

\[ \Delta E^0 = N_A \left( \frac{h c}{\lambda} \right) \left[ \left( \frac{N_{H_2}}{N_{H_2}} \right)^{1/2} - 1 \right] \bar{\omega}_{e, H_2} \] (A.15)

To proceed further note that in amu

\[ M_H = 1.0, \quad M_O = 2.0, \quad M_{H_2} = 36.0, \quad \text{and} \quad M_{H_2} = 39.0 \] (A.16)

and then (A.12) in amu

\[ \frac{N_{H_2}}{N_{H_2}} = \frac{11(35)}{1+35} = 0.97, \quad \text{and} \quad \frac{N_{H_2}}{N_{H_2}} = \frac{2(35)}{2+35} = 4.89 \] (A.17)

Thus

\[ \left( \frac{N_{H_2}}{N_{H_2}} \right)^{1/2} = 0.72 \] (A.18)

Eqs. (A.18) - (A.18) give for Eq. (A.14)

\[ K_{eq}(T) = \left[ \frac{11(35)}{20(130)} \right]^{3/2} \left( \frac{1.97}{0.97} \right) \frac{\left[ 1 - 2 \exp \left( - \frac{\Theta_{H_2}}{T} \right) \right]}{1 - \exp \left( - \frac{\Theta_{H_2}}{T} \right)} \exp \left[ - \frac{\Delta E^0}{R T} \right] \] (A.18)

The above equation may be simplified to

\[ K_{eq}(T) = 0.72 \frac{\left[ 1 - 2 \exp \left( - \frac{\Theta_{H_2}}{T} \right) \right]}{\left[ 1 - \exp \left( - \frac{\Theta_{H_2}}{T} \right) \right]} \exp \left[ - \frac{\Delta E^0}{R T} \right] \] (A.19)
Next let's return to \( \Delta E^0 \). Because of Eq. (A.18), it may be rewritten as

\[
\Delta E^0 = - \frac{R}{2} \left( \frac{hc}{\lambda} \right) (0.28) \tilde{\omega}_{\text{HCl}} = - \frac{R}{2} (0.28) \tilde{\Theta}_{\text{HCl}}. \tag{A.20}
\]

where we have used \( N_0 B = R \) to write \( N_0 (hc/\lambda) \) as \( N_0 \tilde{\omega} (hc/\lambda) = \frac{1}{2} R (hc/\lambda) \) and where we have used \( \tilde{\Theta}_{\text{HCl}} \) to write \( \tilde{\Theta}_{\text{HCl}} \).

Combining Eqs. (A.19) and Eq. (20) yields

\[
K_{eq}(T) = 0.717 \left[ \frac{1 - \exp \left( - \frac{\tilde{\Theta}_{\text{HCl}}}{T} \right)}{1 - \exp \left( - 0.14 \tilde{\Theta}_{\text{HCl}}/T \right)} \right] \exp \left[ + 0.14 \tilde{\Theta}_{\text{HCl}}/T \right]. \tag{A.21}
\]

We next use pages 11 and 12 to give

\[
\tilde{\Theta}_{\text{HCl}} = \frac{hc}{\lambda} \tilde{\omega} \quad \text{or} \quad \tilde{\Theta}_{\text{HCl}}(K) \approx 1.44 \tilde{\omega}_e \text{ (cm}^{-1}) \tag{A.22}.
\]

Thus, from Eqs. (51) and (A.22)

\[
\tilde{\Theta}_{\text{HCl}} = 1.44 \tilde{\omega}_e = 1.44 (2489.7) = 4161 \text{ K}. \tag{A.23}
\]

Thus \( \tilde{\Theta}_{\text{HCl}}/T = 300K = 13.87 \). Consequently Eq. (A.21) becomes

\[
K_{eq}(300K) \approx 0.717 \left[ \frac{1 - \exp \left( - 13.87 \right)}{1 - \exp \left( - 9.99 \right)} \right] \exp \left[ + 1.94 \right] = 0.717 \exp(1.94) \]

\[
K_{eq}(300K) \approx 4.94.
\]