Class 10 Notes

Why is interstellar chemistry important?

1) It produces the critical coolants needed for the collapse phase of star formation.

2) It may play a significant role in producing the molecular building blocks of planetary atmospheres

3) Observationally, it produces tracers of column density, electron density temperataure, UV field, microwave background – but you need to know how different molecules come about in order to derive the physical qualities.

4) Chemical analysis can provide information about physical history – akin to ice cores, because of the range of timescales involved.

Chemical models usually have to make some basic assumptions.

1) defined conditions – UV field, density, temp, CR rate, gas-phase atomic abundances

2) steady-state

You then write down all the relevant reactions and use measured or calculated (or guessed) reaction rates (Fig 1).

## No. 2, 1973 FORMATION OF MOLECULES IN DENSE CLOUDS

rotational transition of  $H^{12}CO^+$ . Confirmation of this speculation would be obtained by observation of the  $J = 1 \rightarrow 0$  transition in  $H^{13}CO^+$ .

## ix) H<sub>2</sub>O, NH<sub>3</sub>

Water and ammonia are predicted by our model to be very abundant. They are produced by dissociative recombination of the ions  $H_3O^+$  and  $NH_4^+$ , respectively:

73.  $OH_3^+ + e \rightarrow H_2O + H$ ,

78.  $\mathrm{NH}_4^+ + e \rightarrow \mathrm{NH}_3 + \mathrm{H}$ .

Water is expected to be the more abundant of the two, with a concentration of approximately  $10^{-2}$  cm<sup>-3</sup>. H<sub>2</sub>O and NH<sub>3</sub> are depleted by reaction with ions such as H<sup>+</sup>, C<sup>+</sup>, HCO<sup>+</sup> and to a lesser extent by condensation on the grains (§ III*c*).

#### x) HCN

Hydrogen cyanide is primarily produced as follows:

50. 
$$C^+ + NH_3 \rightarrow H_2CN^+ + H$$
,  
76.  $H_2CN^+ + e \rightarrow HCN + H$ .

It is destroyed by the reactions:

48. 
$$C^+ + HCN \rightarrow CCN^+ + H$$
,  
33.  $H_3^+ + HCN \rightarrow H_2CN^+ + H_2$ ,

and by condensation on the grain. None of the above rate constants has been measured. We have assumed that reaction 76 yields HCN only. The interesting possibility that HNC could also be formed in this reaction is not considered.

Our calculated HCN densities are  $\sim 10^{-4}$  cm<sup>-3</sup>. These results are in good agreement with observational values.

## xi) H<sub>2</sub>CO

Formaldehyde is unique because of the fact that the reaction

$$H_2 + CO \rightarrow H_2CO$$

is endothermic at low temperatures. Thus it cannot be produced by a scheme, no matter how complex, whose net overall reaction is  $H_2 + CO = H_2CO$ . In our analysis, its production is possible only if we include a slow radiative association step:

65. HCO<sup>+</sup> + H<sub>2</sub>  $\rightarrow$  H<sub>3</sub>CO<sup>+</sup> +  $h\nu$ ,

85. 
$$(H_3CO^+ + e \rightarrow H_2CO + H)$$
.

Formaldehyde is depleted by reaction with ions and condensation on the grain. Since  $H_2$  is so abundant and HCO<sup>+</sup> moderately abundant, the production of  $H_2CO$  is relatively efficient even though it involves such a slow reaction. Our model predicts formaldehyde densities in the range  $10^{-4}$ - $10^{-5}$  cm<sup>-3</sup>, and accounts quite well for observational results on dense clouds (§ IV).



And then solve the coupled equations iteratively until the system relaxes (Fig 2)

Carbon chemistry network from Sternberg & Dalgarro (1995)

Where things get hairier:

1) photo dissociation regions

Why? Because you must solve the chemistry, radiative transfer, and heating/cooling simultaneously.

**<u>Question</u>**: Give some examples from what we have already discussed, of how these things are interconnected.

2) Time dependent cases

Even the simple dense cloud core, with CR ionization and heating, and a few gas-dust collisions, is stongly time dependent.

**Question:** What has been left out of the early gas-phase models?

- a. Freeze-out of molecules onto dust grains. This takes a chemically relevant amount of time, so things change over the whole core lifetime.
- b. collapsing clouds
- c. hot cores gas phase chemistry after sublimation
- d. shock waves liberation of solid materials like Si

Let's not go into the goriest of details but rather try to understand some key principles.

What are some of the critical differences between laboratory chemistry and gas-phase interstellar chemistry?

a. Presence of a UV field.

**Question:** Why is this important?

You can have photodissociation reactions see Table 4.2

**<u>Question</u>**:  $k_{pd} = a \exp \left[-b A_v\right]$ , What does a large b coefficient imply about a molecule?

It implies a high dissociation energy since then the photons are at shorter wavelength, where the dust is more effective.

Note: You calculate these rates by averaging over the field – like photoionization heating rates.

b. Lower temperatures

**Question:** Why is this important?

Activation barriers for neutral-neutral reactions are significant. While the forward-backward balance is established by the energy difference of the reactants and products, the barrier affects the rate

 $A + B \rightleftharpoons C + D + \Delta E$  $\Delta E = -\Delta H \quad (Enthalpy) \qquad \Delta H < 0 \quad \text{for an exothermic reaction. Look at heats of formation.}$ 

 $k = \frac{k_{f}}{k_{b}} exp(\Delta E_{kT})$ 

so even in the absence of barriers, reactions tend to go more one-way of low T. Activation barriers decrease the rate by a factor exp  $\left[-\frac{E_a}{kT}\right]$  with  $E_a/k$  often > 1000. This makes neutral reactions more or less disappear at low T (10K in dense clouds) [look at Table 4.4]

c. Low Density

**Question:** Why is this important?

There is a whole class of reactions that produces an excited and unstable product. In the lab, a collision with another particle takes away the excess energy.

**<u>Ouestion</u>**: How does this occur in the ISM?

In the ISM these are "radiative association" reactions where emission of a photon must stabilize the species

$$A + B \stackrel{k_g}{\underset{k_r}{\longleftarrow}} AB^* \xrightarrow{k_r} AB$$

# d. Presence of ions

In the lab, the gas is extremely neutral whereas, even in the darkest of dark clouds, cosmic rays maintain ionization fractions of  $10^{-6} - 10^{-5}$ .

**Question:** How does this affect the chemistry?

*i)* Ion-molecule reactions are much faster than neutral-neutral reactions, especially considering the activation barriers. Look at Table 4.7

ii) Charge transfer moves ionization to where it can be chemically significant.

H<sup>+</sup> is initially more common than other ions. <u>Why?</u>

Because H is more common.  $O + H^+ \rightarrow O^+ + H$  is the most significant charge exchange. <u>*Why*?</u>

Because ionization energies are almost the same (see HII regions) and so the cross-section is big.

*iii)* Dissociative recombination becomes an important effect in reaction network

<u>Examples</u>:  $HCO^+ + e \rightarrow CO + H$  $H_3^+ + e \rightarrow H + H + H$ 

e. Existence of unsaturated species and long chains.

So how do you figure out the chemical abundances.



set this to zero for all species.

Also, conservation of atoms.

Solve iteratively using standard convergence techniques.