Chemistry: from dark clouds to disks

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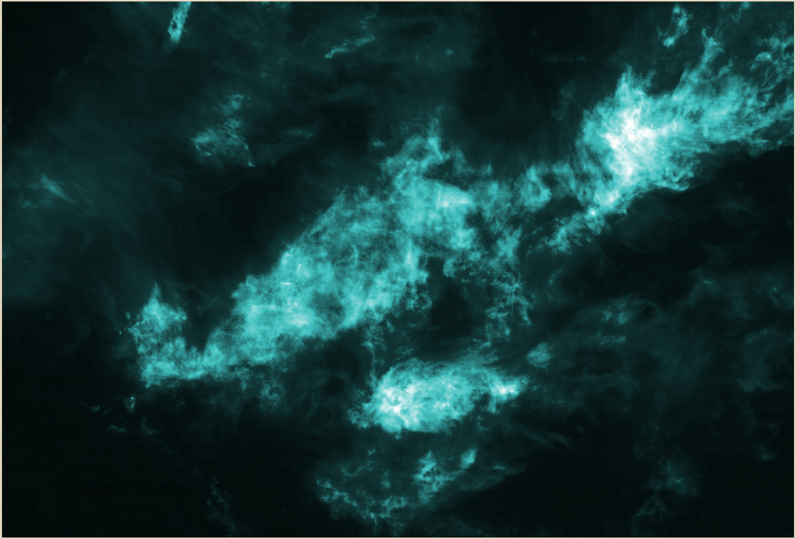
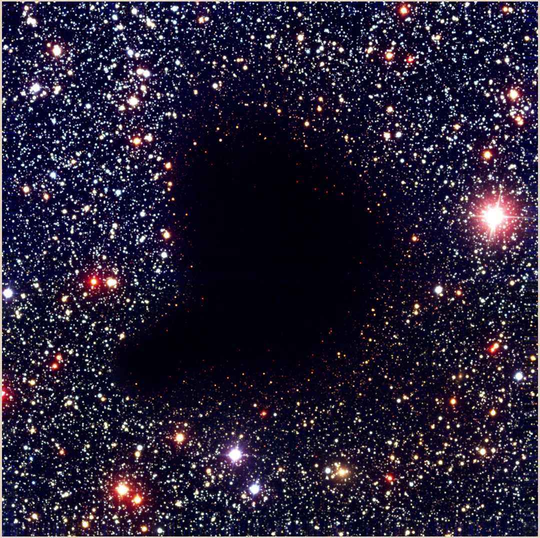
I- The building blocks

1. Introduction & Outline
2. Abundances
3. Interstellar chemistry: general characteristics
4. Gas-phase chemistry
5. Surface chemistry (1)
6. Summary

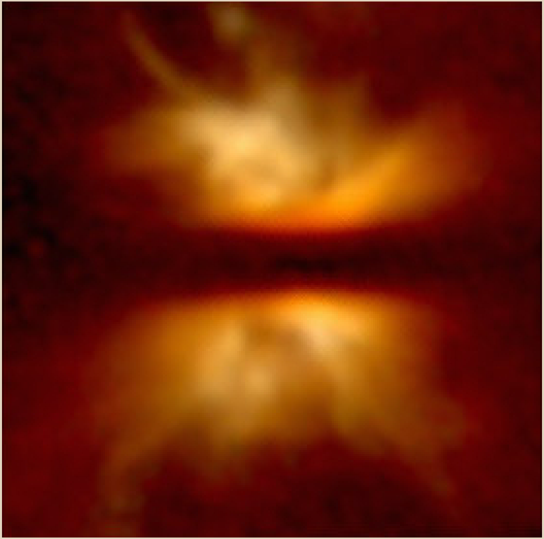
From clouds to stars to planets



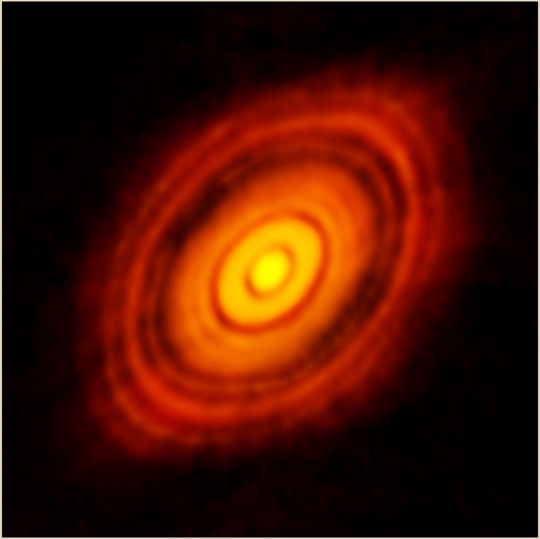
From clouds to stars to planets



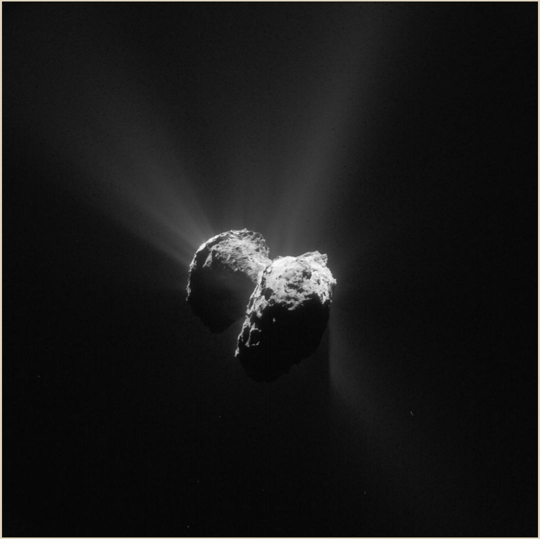
From clouds to stars to planets



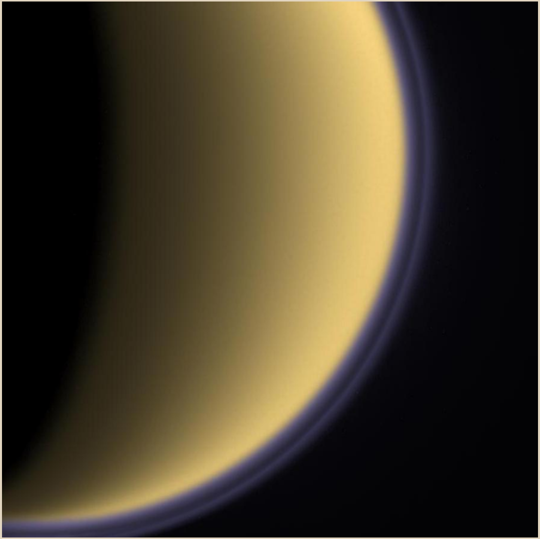
From clouds to stars to planets



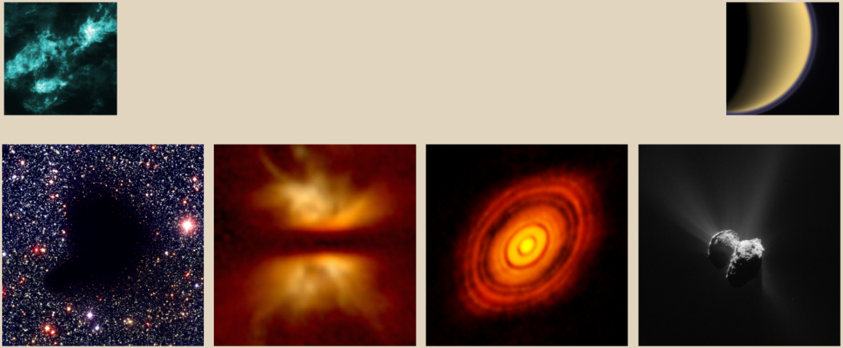
From clouds to stars to planets



From clouds to stars to planets



The interstellar heritage of planetary systems

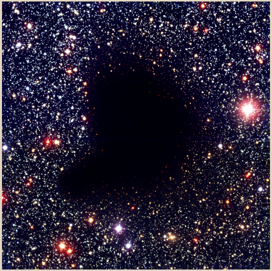


Interstellar phase

Primitive solar system

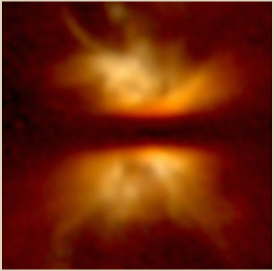
These lectures

Prestellar cores



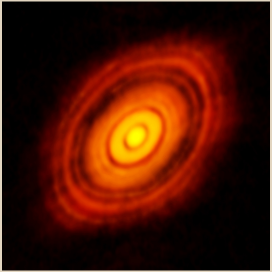
0.1 pc
(2e4 AU, 3e12 km)

Protostars



5000 AU

Protoplanetary disks



100 AU

Why chemistry ?

To know the chemical content of the gas

- What is the Universe made of ?
- Formation/destruction of the species
- Galactic chemical evolution
- Interstellar heritage of planetary systems

To probe the physical conditions

- Kinetic temperature, density, ionization fraction, non-thermal motions
- Trace kinematics through line profiles
- Equation of state: cooling, heating
- To compute physical processes: magnetic fields, multi-fluid

Astrochemistry

Quoting Dalgarno (2008)

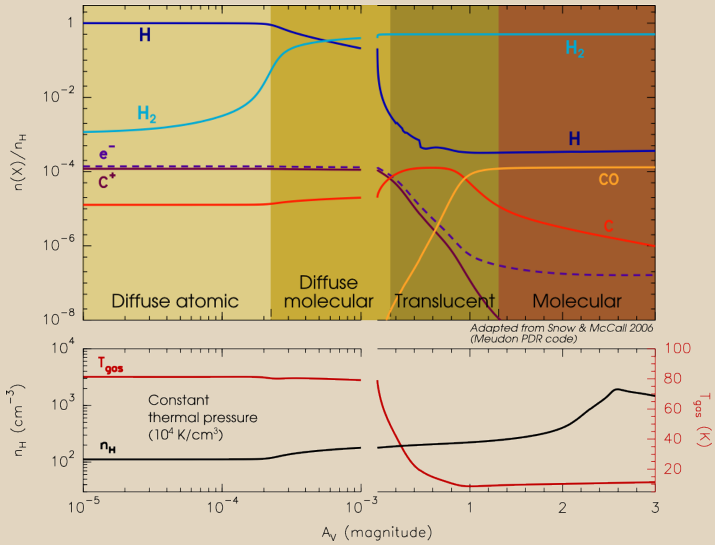
> *"The essential subject matter of astrochemistry is the formation, destruction, and excitation of molecules in astronomical environnements and their influence on the structure, dynamics, and evolution of astronomical objects. The molecules provide powerful diagnostics probes of the ambient physical conditions in which they are found. Progress in astrochemistry rests upon a diversity of observational, experimental, and theoretical skills and a broad knowledge of chemistry and astronomy."*

History of deuterium

- H, D, He, Li, Be (B, and isotopologues)
- History of deuterium: a clue of the history since the Big Bang
- Initial D/H=2.7×10^{-5}
- Today, local ISM: 2.3×10^{-5}
- D/H where/when the PSN formed (-4.6 Gyr, $z = 1.4$): 2.5×10^{-5}
- But Earth oceans: 1.6×10^{-4}
- See C. Burkhardt lecture

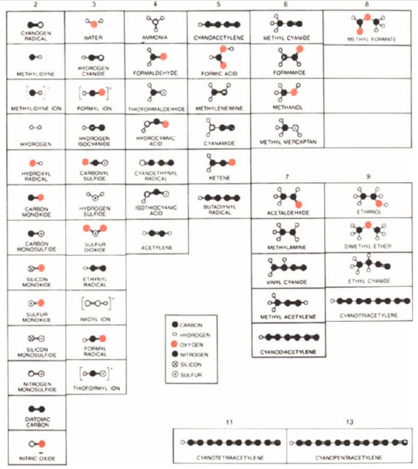
Is D/H telling us something about solar system formation ?

Molecular clouds: the atomic-to-molecular transition



Adapted from Snow & McCall 2006 (Meudon PDR code)

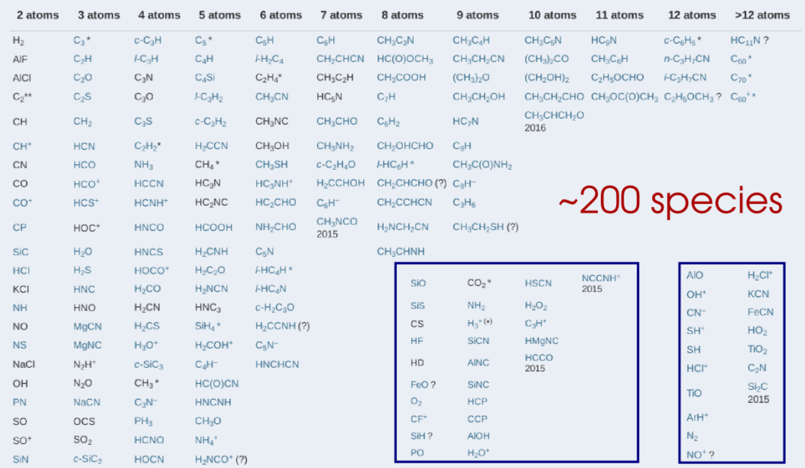
Interstellar species



Prasad et al. (1987)

List of interstellar species in 1987

Interstellar species: a broad choice



2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	>12 atoms
H_2	C_3 *	c-C_3H	C_5 *	C_5H	C_6H	CH_3C_3N	CH_3C_4H	CH_3C_5N	HC_9N	c-C_6H_6 *	$HC_{11}N$?
AlF	C_2H	l-C_3H	C_4H	l-H_2C_4	CH_2CHCN	$HC(O)OCH_3$	CH_3CH_2CN	$(CH_3)_2CO$	CH_3C_6H	n-C_3H_7CN	C_{60} *
AlCl	C_2O	C_3N	C_4Si	C_2H_4*	CH_3C_2H	CH_3COOH	$(CH_3)_2O$	$(CH_2OH)_2$	C_2H_5OCHO	i-C_3H_7CN	C_{70} *
C_2^{**}	C_2S	C_3O	l-C_3H_2	CH_3CN	HC_5N	C_7H	CH_3CH_2OH	CH_3CH_2CHO	$CH_3OC(O)CH_3$	$C_2H_5OCH_3$?	C_{60}^+ *
CH	CH_2	C_3S	c-C_3H_2	CH_3NC	CH_3CHO	C_6H_2	HC_7N	CH_3CHCH_2O 2016			
CH^+	HCN	C_2H_2*	H_2CCN	CH_3OH	CH_3NH_2	CH_2OHCHO	C_8H				
CN	HCO	NH_3	CH_4 *	CH_3SH	c-C_2H_4O	l-HC_6H *	$CH_3C(O)NH_2$				
CO	HCO^+	HCCN	HC_3N	HC_3NH^+	H_2CCHOH	CH_2CHCHO (?)	C_8H^-				
CO^+	HCS^+	$HCNH^+$	HC_2NC	HC_2CHO	C_6H^-	CH_2CCHCN	C_3H_6				
CP	HOC^+	HNCO	HCOOH	NH_2CHO	CH_3NCO 2015	H_2NCH_2CN	CH_3CH_2SH (?)				
SiC	H_2O	HNCS	H_2CNH	C_5N		CH_3CHNH					
HCl	H_2S	$HOCO^+$	H_2C_2O	l-HC_4H *							
KCl	HNC	H_2CO	H_2NCN	l-HC_4N							
NH	HNO	H_2CN	HNC_3	c-H_2C_3O							
NO	MgCN	H_2CS	SiH_4 *	H_2CCNH (?)							
NS	MgNC	H_3O^+	H_2COH^+	C_5N^-							
NaCl	N_2H^+	c-SiC_3	C_4H^-	HNCHCN							
OH	N_2O	CH_3 *	HC(O)CN								
PN	NaCN	C_3N^-	HNCNH								
SO	OCS	PH_3	CH_3O								
SO^+	SO_2	HCNO	NH_4^+								
SiN	c-SiC_2	HOCN	H_2NCO^+ (?)								

~200 species

SiO	CO_2 *	HSCN	$NCCNH^+$ 2015
SiS	NH_2	H_2O_2	
CS	H_3^+ (*)	C_3H^+	
HF	SiCN	HMgNC	
HD	AlNC	HCCO 2015	
FeO ?	SiNC		
O_2	HCP		
CF^+	CCP		
SiH ?	AlOH		
PO	H_2O^+		

AlO	H_2Cl^+
OH^+	KCN
CN^-	FeCN
SH^+	HO_2
SH	TiO_2
HCl^+	C_2N
TiO	Si_2C 2015
ArH^+	
N_2	
NO^+ ?	

CDMS list of ISM species; see also `www.astrochymist.org`

This lecture

Today

- General characteristics of interstellar chemistry
- The elemental abundances (unusual aspects of)
- Overview of gas-phase processes and orders of magnitudes
- The interplay between theory, models, and observations

Tomorrow

- Chemistry from cores to disks: similarities and differences
- Time-dependent vs steady-state: influence of the initial conditions
- Isotopic ratios as tracers of the history

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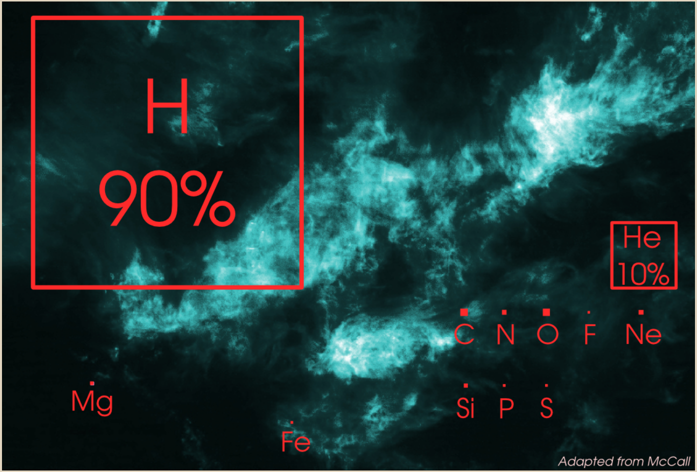
Abundances

- Absolute quantities (cm^{-3})
- Relative quantities (abundances, or concentrations)
- Chemical models compute local densities
- Observations provide line-of-sight quantities (column densities)
- Column density ratios: more robust

The astrochemist table of elements



Adapted from McCall

Interstellar chemistry is dominated by hydrogen

Elemental abundances

- Total amount of element X is its *elemental* abundance
- Abundances are usually measured wrt H nuclei

$$\boxed{[\mathrm{X}] = n(\mathrm{X})/n_{\mathrm{H}}}$$

- $n_{\mathrm{H}} = n(\mathrm{H}) + 2n(\mathrm{H}_2) + n(\mathrm{H}^+) + 2n(\mathrm{H}_2^+) + \ldots$
- Warning: in dense, fully molecular gas, some authors use abundances wrt H_2 molecules

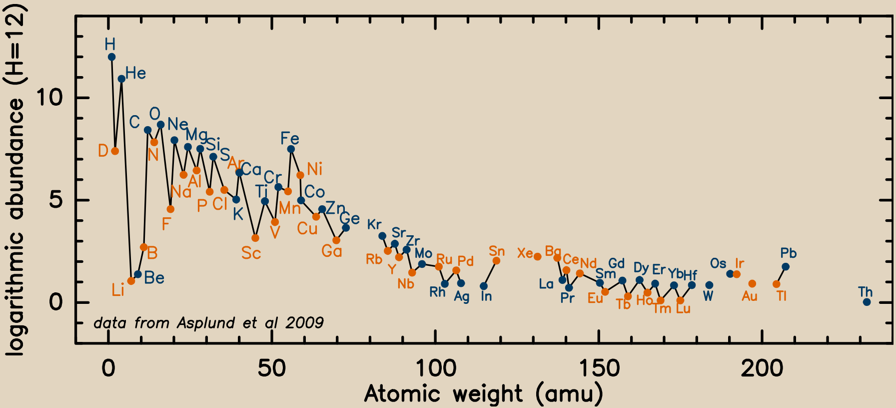
$$n(\mathrm{X})/n(\mathrm{H}_2) = 2n(\mathrm{X})/n_{\mathrm{H}}$$

- Advice: always use wrt H nuclei; in any case, make it explicit (and say it in your captions)
- In this lecture: wrt n_{H}

Cosmic abundances

- Elemental abundances are functions of space and time: galactic chemical evolution (GCE) models (Matteucci 2012)
- So-called *cosmic abundances* or *cosmic abundance standard*
- Derived from observations of stellar atmospheres
- Quite model-dependent: although precise, not necessarily accurate !
- General reference: Asplund et al. (2009)
- Related lectures: M. Gounelle, H. Leroux, C. Engrand, L. Nittler

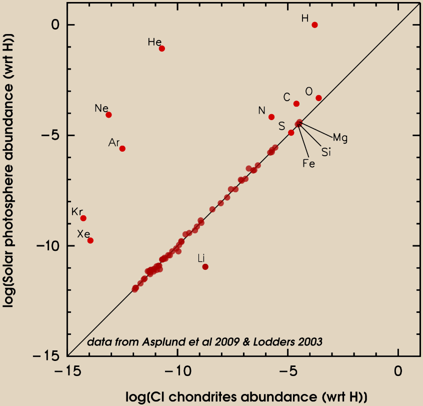
Solar abundances (1): photosphere



data from Asplund et al 2009

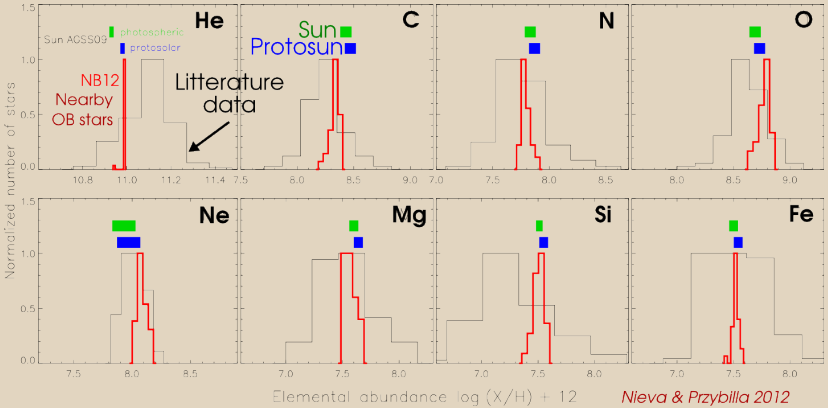
- Sun photosphere + (1D–3D) radiative transfer modeling
- Representative of the abundances -4.6 Gyr at the Sun's birthplace

Solar abundances (2): CI chondrites



- Mass spectroscopy of primitive meteorites; more direct
- Most primitive are CI chondrites
- Do not trace highly volatiles (H, C, N, O, noble gases); often normalized to Si (non volatile)
- General reference: Lodders (2003, 2010)
- Lectures from M. Gounelle, L. Nittler, F. Ciesla, C. Engrand

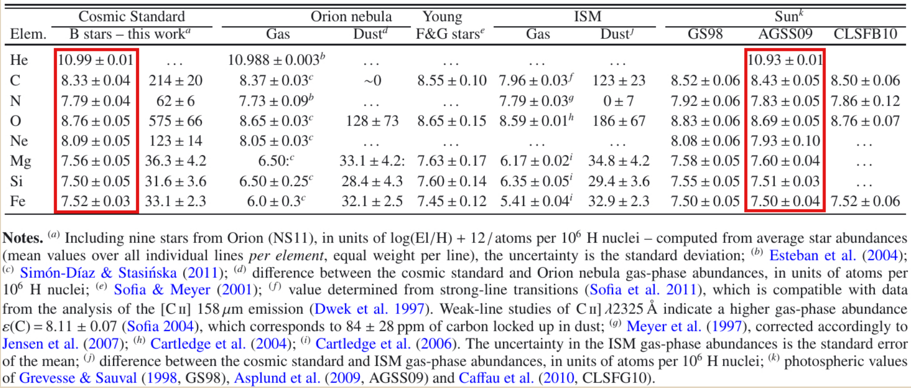
Cosmic Abundance Standard (CAS)



- local ISM abundances from B-type stars (Nieva & Przybilla 2012)
- radiative transfer modeling

Is the Sun representative of the present-day local ISM ?

Cosmic Abundance Standard (CAS)

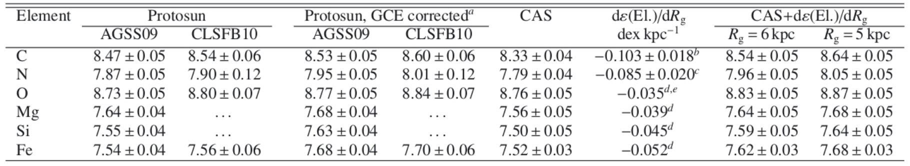


	Cosmic Standard		Orion nebula		Young	ISM		Sun[k]		
Elem.	B stars – this work[a]		Gas	Dust[d]	F&G stars[e]	Gas	Dust[j]	GS98	AGSS09	CLSFB10
He	10.99 ± 0.01	…	10.988 ± 0.003[b]	…	…	…	…		10.93 ± 0.01	
C	8.33 ± 0.04	214 ± 20	8.37 ± 0.03[c]	∼0	8.55 ± 0.10	7.96 ± 0.03[f]	123 ± 23	8.52 ± 0.06	8.43 ± 0.05	8.50 ± 0.06
N	7.79 ± 0.04	62 ± 6	7.73 ± 0.09[b]	…	…	7.79 ± 0.03[g]	0 ± 7	7.92 ± 0.06	7.83 ± 0.05	7.86 ± 0.12
O	8.76 ± 0.05	575 ± 66	8.65 ± 0.03[c]	128 ± 73	8.65 ± 0.15	8.59 ± 0.01[h]	186 ± 67	8.83 ± 0.06	8.69 ± 0.05	8.76 ± 0.07
Ne	8.09 ± 0.05	123 ± 14	8.05 ± 0.03[c]	…	…	…	…	8.08 ± 0.06	7.93 ± 0.10	…
Mg	7.56 ± 0.05	36.3 ± 4.2	6.50:[c]	33.1 ± 4.2:	7.63 ± 0.17	6.17 ± 0.02[i]	34.8 ± 4.2	7.58 ± 0.05	7.60 ± 0.04	…
Si	7.50 ± 0.05	31.6 ± 3.6	6.50 ± 0.25[c]	28.4 ± 4.3	7.60 ± 0.14	6.35 ± 0.05[i]	29.4 ± 3.6	7.55 ± 0.05	7.51 ± 0.03	…
Fe	7.52 ± 0.03	33.1 ± 2.3	6.0 ± 0.3[c]	32.1 ± 2.5	7.45 ± 0.12	5.41 ± 0.04[i]	32.9 ± 2.3	7.50 ± 0.05	7.50 ± 0.04	7.52 ± 0.06

Notes. (a) Including nine stars from Orion (NS11), in units of log(El/H) + 12 / atoms per 10^6 H nuclei – computed from average star abundances (mean values over all individual lines *per element*, equal weight per line), the uncertainty is the standard deviation; (b) Esteban et al. (2004); (c) Simón-Díaz & Stasińska (2011); (d) difference between the cosmic standard and Orion nebula gas-phase abundances, in units of atoms per 10^6 H nuclei; (e) Sofia & Meyer (2001); (f) value determined from strong-line transitions (Sofia et al. 2011), which is compatible with data from the analysis of the [C II] 158 μm emission (Dwek et al. 1997). Weak-line studies of C II λ2325 Å indicate a higher gas-phase abundance $\varepsilon(C) = 8.11 \pm 0.07$ (Sofia 2004), which corresponds to 84 ± 28 ppm of carbon locked up in dust; (g) Meyer et al. (1997), corrected accordingly to Jensen et al. (2007); (h) Cartledge et al. (2004); (i) Cartledge et al. (2006). The uncertainty in the ISM gas-phase abundances is the standard error of the mean; (j) difference between the cosmic standard and ISM gas-phase abundances, in units of atoms per 10^6 H nuclei; (k) photospheric values of Grevesse & Sauval (1998, GS98), Asplund et al. (2009, AGSS09) and Caffau et al. (2010, CLSFG10).

Metallicity of the Sun unexpectedly high

Present-day local ISM abundances



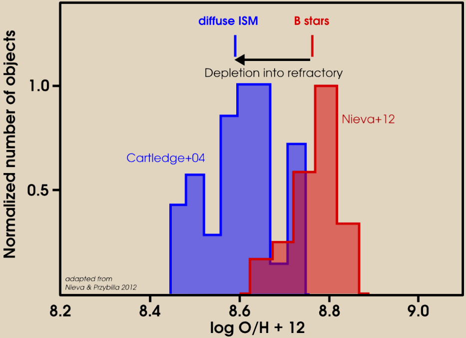
Element	Protosun		Protosun, GCE corrected[a]		CAS	$d\varepsilon(\mathrm{El.})/dR_g$	CAS+$d\varepsilon(\mathrm{El.})/dR_g$	
	AGSS09	CLSFB10	AGSS09	CLSFB10		dex kpc^{-1}	$R_g = 6$ kpc	$R_g = 5$ kpc
C	8.47 ± 0.05	8.54 ± 0.06	8.53 ± 0.05	8.60 ± 0.06	8.33 ± 0.04	−0.103 ± 0.018[b]	8.54 ± 0.05	8.64 ± 0.05
N	7.87 ± 0.05	7.90 ± 0.12	7.95 ± 0.05	8.01 ± 0.12	7.79 ± 0.04	−0.085 ± 0.020[c]	7.96 ± 0.05	8.05 ± 0.05
O	8.73 ± 0.05	8.80 ± 0.07	8.77 ± 0.05	8.84 ± 0.07	8.76 ± 0.05	−0.035[d,e]	8.83 ± 0.05	8.87 ± 0.05
Mg	7.64 ± 0.04	…	7.68 ± 0.04	…	7.56 ± 0.05	−0.039[d]	7.64 ± 0.05	7.68 ± 0.05
Si	7.55 ± 0.04	…	7.63 ± 0.04	…	7.50 ± 0.05	−0.045[d]	7.59 ± 0.05	7.64 ± 0.05
Fe	7.54 ± 0.04	7.56 ± 0.06	7.68 ± 0.04	7.70 ± 0.06	7.52 ± 0.03	−0.052[d]	7.62 ± 0.03	7.68 ± 0.03

- Solar photosphere not necessarily representative of the local ISM
- Birthplace of the Sun is unknown
- Outward migration more likely (Nieva & Przybilla 2012; Minchev et al. 2013; Hily-Blant et al. 2017) but see Martínez-Barbosa et al. (2015)

Chemical homogeneity

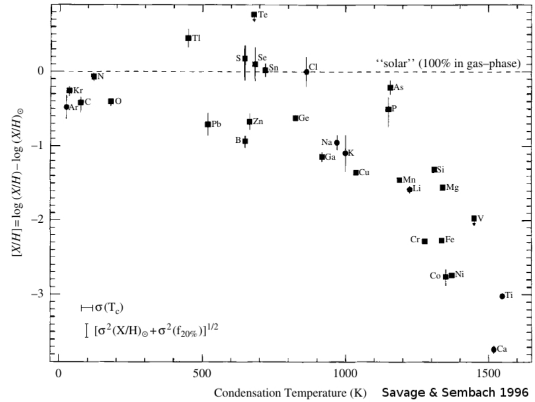
- Local ISM (within 1.5 kpc) is chemically homogeneous at a 10% level
- Allows meaningful comparisons between star and planet forming regions in the local ISM
- Choice of a set of elemental abundances: sun, B-stars
- Recommended litterature: Sofia & Meyer (2001); Asplund et al. (2009); Nieva & Przybilla (2012)

Refractories and volatiles



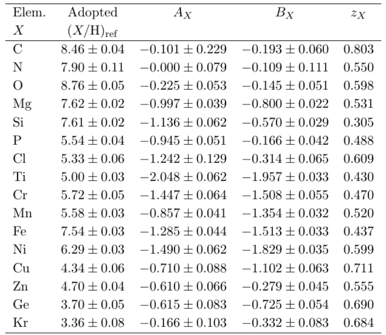
- In astrochemistry: refractory ≡ dust (condensation temp.)
- Depletion of elements into refractory in the diffuse ISM
- Dust abundances: indirect estimates (extinction models)

Depletion of elements



Savage & Sembach 1996

Refractories and volatiles



Elem. X	Adopted $(X/\mathrm{H})_{\mathrm{ref}}$	A_X	B_X	z_X
C	8.46 ± 0.04	-0.101 ± 0.229	-0.193 ± 0.060	0.803
N	7.90 ± 0.11	-0.000 ± 0.079	-0.109 ± 0.111	0.550
O	8.76 ± 0.05	-0.225 ± 0.053	-0.145 ± 0.051	0.598
Mg	7.62 ± 0.02	-0.997 ± 0.039	-0.800 ± 0.022	0.531
Si	7.61 ± 0.02	-1.136 ± 0.062	-0.570 ± 0.029	0.305
P	5.54 ± 0.04	-0.945 ± 0.051	-0.166 ± 0.042	0.488
Cl	5.33 ± 0.06	-1.242 ± 0.129	-0.314 ± 0.065	0.609
Ti	5.00 ± 0.03	-2.048 ± 0.062	-1.957 ± 0.033	0.430
Cr	5.72 ± 0.05	-1.447 ± 0.064	-1.508 ± 0.055	0.470
Mn	5.58 ± 0.03	-0.857 ± 0.041	-1.354 ± 0.032	0.520
Fe	7.54 ± 0.03	-1.285 ± 0.044	-1.513 ± 0.033	0.437
Ni	6.29 ± 0.03	-1.490 ± 0.062	-1.829 ± 0.035	0.599
Cu	4.34 ± 0.06	-0.710 ± 0.088	-1.102 ± 0.063	0.711
Zn	4.70 ± 0.04	-0.610 ± 0.066	-0.279 ± 0.045	0.555
Ge	3.70 ± 0.05	-0.615 ± 0.083	-0.725 ± 0.054	0.690
Kr	3.36 ± 0.08	-0.166 ± 0.103	-0.332 ± 0.083	0.684

- Jenkins (2009, 2014): $A_X \sim$ consumption rate, $B_X \sim$ propensity towards depletion ($z_X \sim$ scaling factor)
- Not all elements have the same propensity towards depletion

ISM: Volatiles = cosmic - refractory = gas + ice

Initial conditions

- Elements are partitioned among species by chemical processes
- Sum of all abundances of that element is its elemental abundance
- The different species may be called *reservoirs*
- For some species, one reservoir dominates
- E.g. in moderately dense clouds ($n_{\mathrm{H}} \approx 10^3\,\mathrm{cm}^{-3}$), the main reservoir of the carbon element is CO, and $n(\mathrm{CO}) \lesssim n_{\mathrm{tot}}(\mathrm{C})$

Initial conditions = elemental abundances + initial partitioning

Recommended values

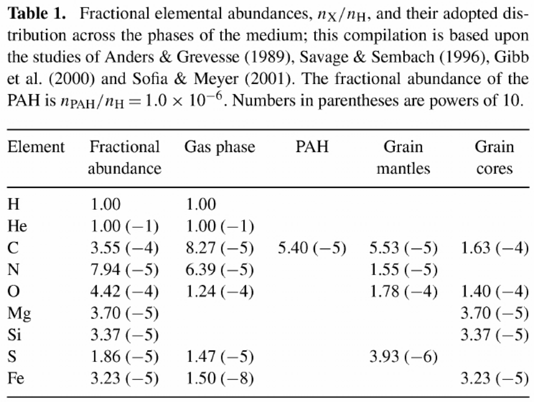


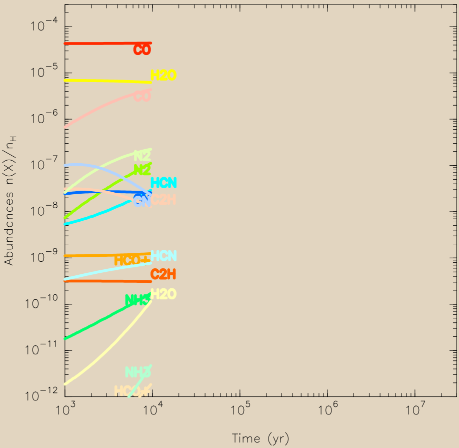
Table 1. Fractional elemental abundances, n_X/n_H, and their adopted distribution across the phases of the medium; this compilation is based upon the studies of Anders & Grevesse (1989), Savage & Sembach (1996), Gibb et al. (2000) and Sofia & Meyer (2001). The fractional abundance of the PAH is $n_{PAH}/n_H = 1.0 \times 10^{-6}$. Numbers in parentheses are powers of 10.

Element	Fractional abundance	Gas phase	PAH	Grain mantles	Grain cores
H	1.00	1.00			
He	1.00 (−1)	1.00 (−1)			
C	3.55 (−4)	8.27 (−5)	5.40 (−5)	5.53 (−5)	1.63 (−4)
N	7.94 (−5)	6.39 (−5)		1.55 (−5)	
O	4.42 (−4)	1.24 (−4)		1.78 (−4)	1.40 (−4)
Mg	3.70 (−5)				3.70 (−5)
Si	3.37 (−5)				3.37 (−5)
S	1.86 (−5)	1.47 (−5)		3.93 (−6)	
Fe	3.23 (−5)	1.50 (−8)			3.23 (−5)

Flower & Pineau des Forêts (2003)

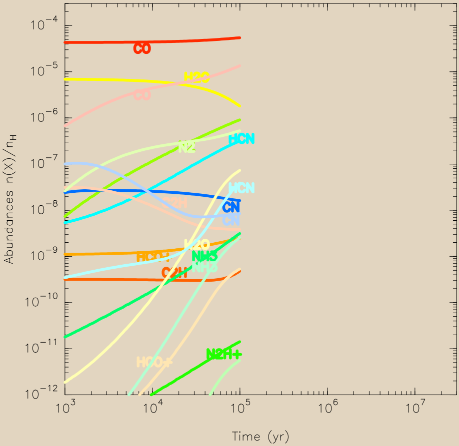
- Not a unique choice
- consider varying the C/O, N/N_2 etc (Le Gal et al. 2014)
- Advice: always quote the adopted values in the article

Influence of the initial partitioning: example



- One set of elemental abundances
- Two sets of initial partitioning (e.g. corresponding to slightly different $A_{\rm V}$)
- *molecular* case:
  - H_2=1
  - C^+=1
  - O=1
- *mixed* case:
  - H_2=67%
  - C/C^+=1
  - O/H_2O=1
- Note: identical steady-state

Influence of the initial partitioning: example



- One set of elemental abundances
- Two sets of initial partitioning (e.g. corresponding to slightly different $A_{\rm V}$)
- *molecular* case:
  - H_2=1
  - C^+=1
  - O=1
- *mixed* case:
  - H_2=67%
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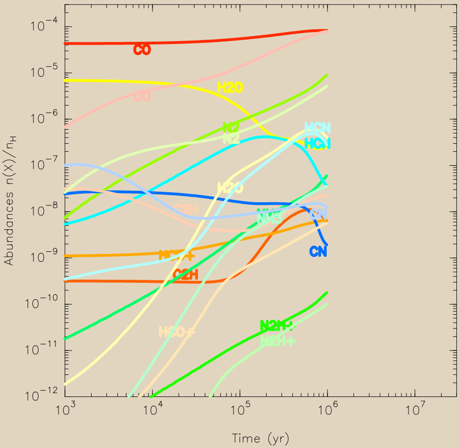
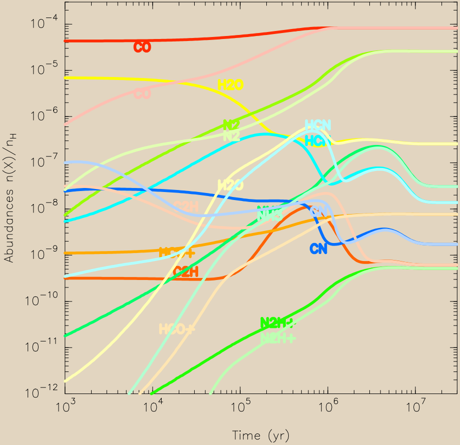


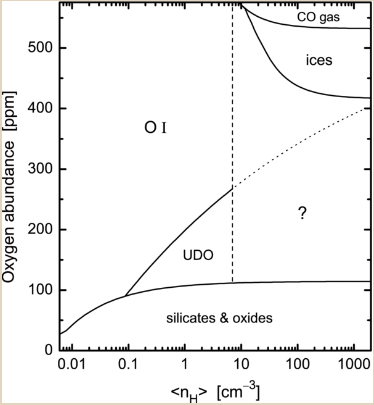
- One set of elemental abundances
- Two sets of initial partitioning (e.g. corresponding to slightly different $A_{\rm V}$)
- *molecular* case:
    - $\mathrm{H_2}$=1
    - C^+=1
    - O=1
- *mixed* case:
    - $\mathrm{H_2}$=67%
    - $\mathrm{C/C}^+$=1
    - $\mathrm{O/H_2O}$=1
- Note: identical steady-state

Influence of the initial partitioning: example



- One set of elemental abundances
- Two sets of initial partitioning (e.g. corresponding to slightly different A_V)
- *molecular* case:
  - H_2=1
  - C^+=1
  - O=1
- *mixed* case:
  - H_2=67%
  - C/C^+=1
  - O/H_2O=1
- Note: identical steady-state

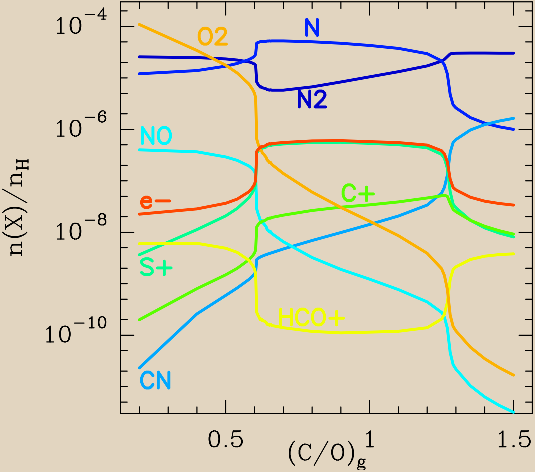
Missing reservoirs



Whittet (2010)

- Oxygen: on third can not be accounted for by known reservoirs
- Carbon: dust (200–300 ppm) + volatile (100–200 ppm), total (200–300 ppm)

Influence of the elemental abundances: the C/O ratio



Variation of the gas-phase elemental abundance of C and O

I- The building blocks

Interstellar chemistry is ruled by kinetics

- Takes place in the CNM: from diffuse ($n_{\rm H} \sim 100\,{\rm cm}^{-3}$) to dense ($n_{\rm H} > 10^4\,{\rm cm}^{-3}$) clouds
- Low density: no time to reach equilibrium
- IS chemistry is driven by kinetics

Kinetics vs equilibrium

$$\mathsf{AB} + \mathsf{C} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathsf{A} + \mathsf{BC}$$

- Thermodynamics:

$$K(T) = \frac{[A] \cdot [BC]}{[AB] \cdot [C]}$$

- Kinetics:

$$\frac{dn(\mathrm{A})}{dt} = -\frac{dn(\mathrm{AB})}{dt} = k(T)n(\mathrm{AB})n(\mathrm{C})$$

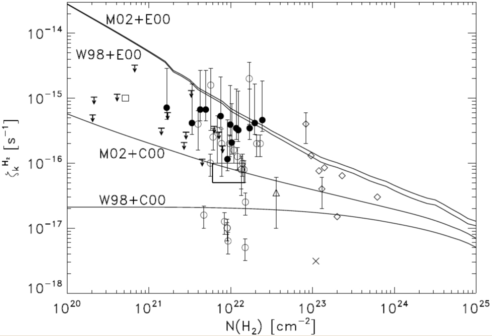
- Detailed balance ($t \to \infty$):

$$K = \frac{k_f}{k_r} \propto \exp(-\Delta G/kT)$$

Consequences

- Low temperature: exothermic reactions dominate (ion-neutral)
- Backward reactions not included: $t \to \infty$ does not converge towards equilibrium (molecular clouds lifetime is limited)
- steady-state $\neq$ equilibrium
- Example: HCN/HNC ≈ 1 in cold clouds; HCN is 65.5 kJ/mol below HNC, equilibrated abundance ratio would be HCN/HNC$= 10^{170}$
- Example: carbon is mostly in CO; but $[\mathrm{CH_4}][\mathrm{H_2O}]/[\mathrm{CO}][\mathrm{H_2}]^3 > 10^{500}$ at equilibrium through $\mathrm{CO} + 3\,\mathrm{H_2O} \longrightarrow \mathrm{CH_4} + \mathrm{H_2O}$;
- time-dependent/steady-state, various timescales (from yr to few Myr)
- $\tau \sim 1/(k(T) n_{\mathrm{H}}[\mathrm{X}]) \sim [\,10^{-11}\,10^{4}\,10^{-5}]^{-1} \sim 0.1$ Myr

Ionization

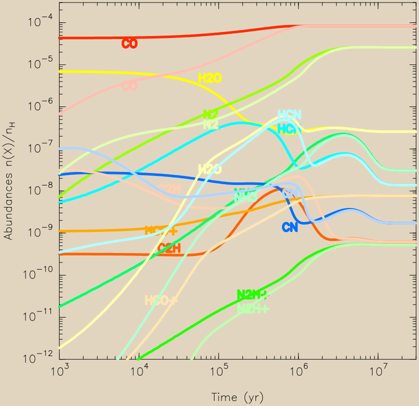


- Driven by cosmic ray ionization $\zeta \approx 10^{-17} - 10^{-16}\,\mathrm{s}^{-1}$

$$x_e = n_e/n_\mathrm{H} \propto (\zeta/n_\mathrm{H})^{0.5}$$

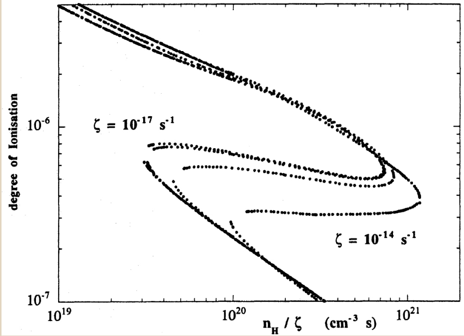
- in the deep interior: secondary photons (fluorescence of collisionally excited H_2)

Steady-state: complications



- In most cases, steady-state does not depend on history
- In some instances, steady-state does depend on history: bistable character

Steady-state: complications



Le Bourlot et al. (1995)

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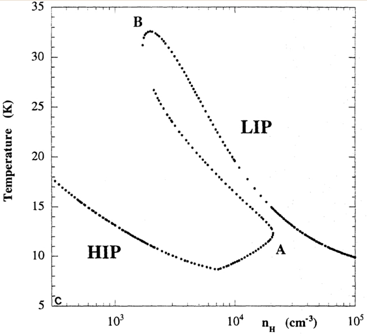
Steady-state: complications



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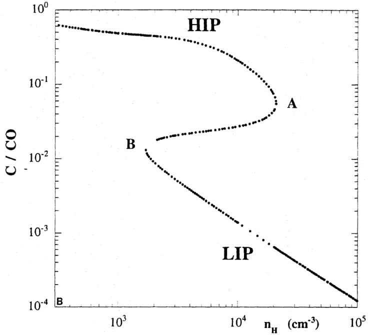
Steady-state: complications



Le Bourlot et al. (1995)

- In most cases, steady-state does not depend on history
- In some instances, steady-state does depend on history: bistable character

Gas and dust

- Two components: volatiles (gas+ice) and refractory (dust)
- Dust (1% in mass) but pivotal role: thermal balance, chemistry, dynamics
- Charge state (or ionization fraction): controls dissipative effects (Ohm, Hall, etc), coupling with magnetic fields
- Charge: both gas and dust
- Ionization: cosmic rays + secondary photons, direct UV

Control parameters

- Temperature (kinetic rate coefficients, evaporation)
- Density (frequency of collisions, ionization, freeze-out)
- Elemental abundances (C/O ratio, sulfur, etc)
- Ionization: UV, cosmic-rays
- External UV flux (ISRF) (diffuse ISM, upper layers in disks)
- Cosmic-ray ionization rate ζ (essentially through ζ/n_{H})

Chemistry in dilute interstellar gas

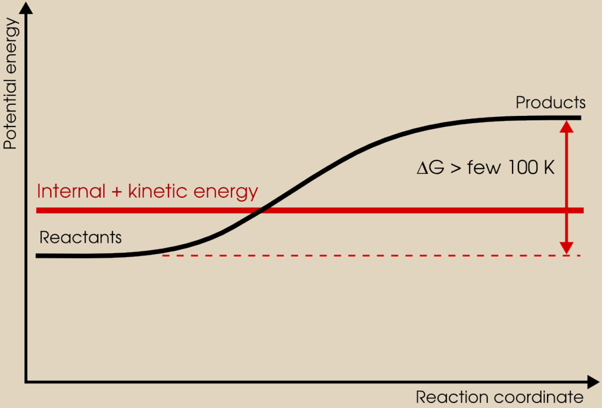
- Dominated by bi-molecular collisions and uni-molecular
- No three-body collisions
- During the collision, formation of an activated complex $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{AB}^*$, lifetime $\sim 10^{-12}$ s
- Stabilize complex: remove energy; otherwise $\mathrm{AB}^* \longrightarrow \mathrm{A} + \mathrm{B}$ will occur
- Third-body collision most unlikely
- Only reactions involving molecules: $\mathrm{AB} + \mathrm{C} \longrightarrow \mathrm{A} + \mathrm{BC}$
- Emission of a photon: $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{AB} + h\nu$

Bi-molecular collisions

$$\mathsf{AB} + \mathsf{C} \xrightarrow{k} \mathsf{A} + \mathsf{BC}, \quad k(T)\ \mathrm{cm^3\,s^{-1}}$$

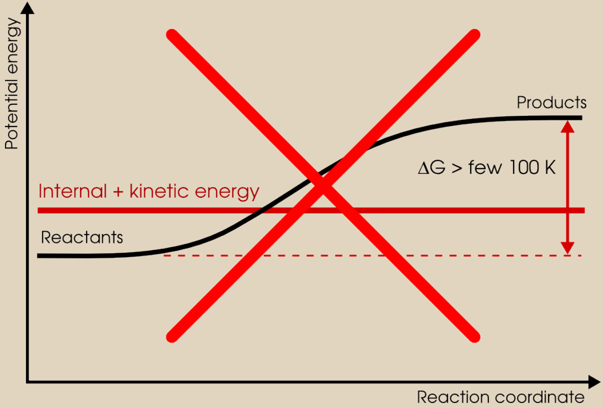
- low density: only bi-molecular collisions
- reaction involves inelastic collisions with destruction/creation of bonds
- the overall energy balance involves primarily the formation enthalpy: $\Delta G = \Delta H - T\Delta S \approx \Delta H$ at low T
- exoergic reaction: ΔG larger than a few 100 K
- endoergic reaction: ΔG smaller than a few -100 K
- thermoneutral reaction: $|\Delta G|$ within a few 100 K
- kinetic rate are measured and/or computed theoretically

Exoergic reactions only



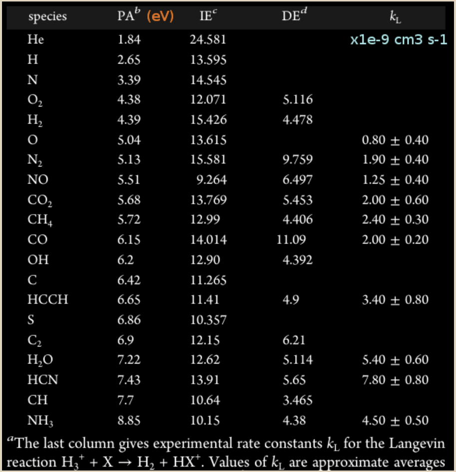
- Endoergic reactions

Exoergic reactions only



- Endoergic reactions
- ΔG too large: are not considered

Energetic properties of principal species



species	PA^b (eV)	IE^c	DE^d	k_L
He	1.84	24.581		x1e-9 cm3 s-1
H	2.65	13.595		
N	3.39	14.545		
O_2	4.38	12.071	5.116	
H_2	4.39	15.426	4.478	
O	5.04	13.615		0.80 ± 0.40
N_2	5.13	15.581	9.759	1.90 ± 0.40
NO	5.51	9.264	6.497	1.25 ± 0.40
CO_2	5.68	13.769	5.453	2.00 ± 0.60
CH_4	5.72	12.99	4.406	2.40 ± 0.30
CO	6.15	14.014	11.09	2.00 ± 0.20
OH	6.2	12.90	4.392	
C	6.42	11.265		
HCCH	6.65	11.41	4.9	3.40 ± 0.80
S	6.86	10.357		
C_2	6.9	12.15	6.21	
H_2O	7.22	12.62	5.114	5.40 ± 0.60
HCN	7.43	13.91	5.65	7.80 ± 0.80
CH	7.7	10.64	3.465	
NH_3	8.85	10.15	4.38	4.50 ± 0.50

[a] The last column gives experimental rate constants k_L for the Langevin reaction $H_3^+ + X \rightarrow H_2 + HX^+$. Values of k_L are approximate averages

Oka (2013)

- PA: proton affinity
- IE: ionization energy
- DE=dissociation energy
- $X + H_3^+ \longrightarrow XH^+ + H_2 + \Delta E$, $\Delta E = \text{PA(X)-PA(H}_2\text{)}$
- H_3^+ is a proton donnor

General references

- Not possible to acknowledge the wide field of astrochemistry
- Partial choice of most valuable readings:
    - Very general: Watson (1976), Klemperer (2006), Bergin (2009), Oka (2013)
    - Cold cloud chemistry foundation: Herbst & Klemperer (1973), Prasad et al. (1987)
    - Complex organic molecules: Herbst & van Dishoeck (2009)
    - A. Dalgarno†, J. Black, E. van Dishoeck

I- The building blocks

1. Introduction & Outline
2. Abundances
3. Interstellar chemistry: general characteristics
4. Gas-phase chemistry
5. Surface chemistry (1)
6. Summary

Overview of astrochemical modelling

Chemical network

- set of reactive collisions + ionization, etc
- historical databases: Herbst& Klemperer 1977, Prasad & Huntress 1980, Millar et al 1991
- derived general databases: KIDA (inherited from OSU), UMIST

Numerical solver

- time-dependent: stiff 1st order ODE (`DVODE`)
- steady-state: zero-finding algorithms (e.g. Newton-Raphson)

Boundary conditions

- Elemental abundances and initial partitioning

Types of reactions and orders of magnitude

Type	Example	$k(T)$
CR ionization	$He + CRP \longrightarrow He^+ + e^-$	10^{-16}–$10^{-17}\,\mathrm{s^{-1}}$
ion-neutral	$CO + H_3^+ \longrightarrow HCO^+ + H_2$	$10^{-9}\,\mathrm{cm^3\,s^{-1}}$
neutral-neutral	$N + CH \longrightarrow CN + H$	$10^{-11}\,\mathrm{cm^3\,s^{-1}}$
Charge exchange	$O^+ + H \longrightarrow O + H^+$	$10^{-10}\,\mathrm{cm^3\,s^{-1}}$
Dissociative recombination	$NH_4^+ + e^- \longrightarrow NH_3 + H$	$10^{-6}\,\mathrm{cm^3\,s^{-1}}$
Radiative recombination	$C^+ + e^- \longrightarrow C + h\nu$	$10^{-12}\,\mathrm{cm^3\,s^{-1}}$
Radiative association	$C^+ + H_2 \longrightarrow CH_2^+ + h\nu$	$10^{-17}\,\mathrm{cm^3\,s^{-1}}$
Photoionization	$C + h\nu \longrightarrow C^+ + H$	$10^{-9}\exp(-\gamma A_\mathrm{V})\,\mathrm{cm^3\,s^{-1}}$
Photodissociation	$H_2O + h\nu \longrightarrow OH + H$	$10^{-9}\exp(-\gamma A_\mathrm{V})\,\mathrm{cm^3\,s^{-1}}$

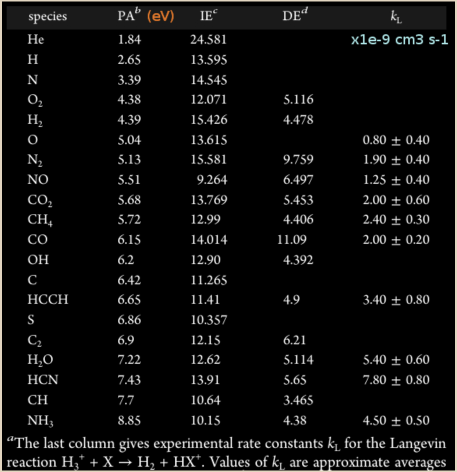
Langevin rates

- proton-hop reaction: $H_2 + H_2^+ \longrightarrow H_3^+ + H + 1.74\mathrm{eV}$
- ion-dipole: key factor = polarizability α (cm^3)
- approaching H_2^+ polarizes H_2 inducing a dipole moment
- charge-induced dipole potential, or Langevin potential: $V_L = -\alpha e^2/2r^4$
- cross-section: $\sigma_L = \pi r_L^2 = 2\pi \frac{e}{v}(\alpha/\mu)^{1/2}$, μ: reduced mass
- impact parameter $b < r_L$ leads to reaction
- Langevin rate (cgs units): $k_L = \int v\sigma_L(v)f(v)dv$:

$$k_L = 2\pi e(\alpha/\mu)^{1/2}, \qquad \alpha \approx 1\text{Å}^3$$

- $k_L \approx 10^{-9}\ \mathrm{cm^3\,s^{-1}}$, for all systems
- k_L: ind. of T, hence dominate at low-T

Langevin rates



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[a] The last column gives experimental rate constants k_L for the Langevin reaction $H_3^+ + X \rightarrow H_2 + HX^+$. Values of k_L are approximate averages

Oka (2013)

Langevin rates and H_3^+ drive interstellar chemistry

Langevin rates

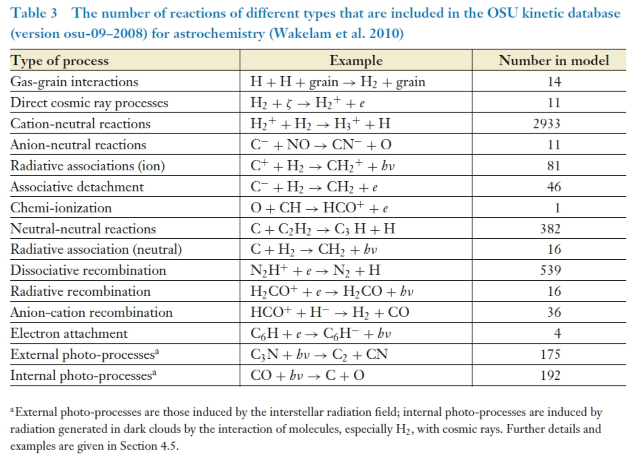


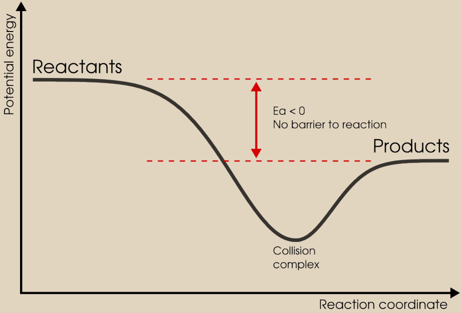
Table 3 The number of reactions of different types that are included in the OSU kinetic database (version osu-09–2008) for astrochemistry (Wakelam et al. 2010)

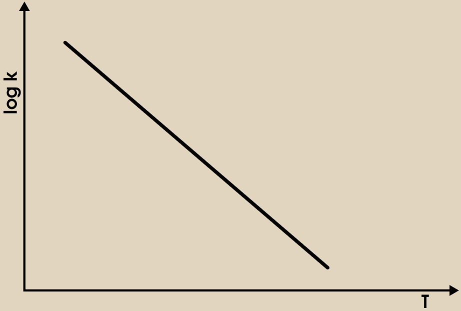
Type of process	Example	Number in model
Gas-grain interactions	$H + H + \text{grain} \rightarrow H_2 + \text{grain}$	14
Direct cosmic ray processes	$H_2 + \zeta \rightarrow H_2{}^+ + e$	11
Cation-neutral reactions	$H_2{}^+ + H_2 \rightarrow H_3{}^+ + H$	2933
Anion-neutral reactions	$C^- + NO \rightarrow CN^- + O$	11
Radiative associations (ion)	$C^+ + H_2 \rightarrow CH_2{}^+ + h\nu$	81
Associative detachment	$C^- + H_2 \rightarrow CH_2 + e$	46
Chemi-ionization	$O + CH \rightarrow HCO^+ + e$	1
Neutral-neutral reactions	$C + C_2H_2 \rightarrow C_3H + H$	382
Radiative association (neutral)	$C + H_2 \rightarrow CH_2 + h\nu$	16
Dissociative recombination	$N_2H^+ + e \rightarrow N_2 + H$	539
Radiative recombination	$H_2CO^+ + e \rightarrow H_2CO + h\nu$	16
Anion-cation recombination	$HCO^+ + H^- \rightarrow H_2 + CO$	36
Electron attachment	$C_6H + e \rightarrow C_6H^- + h\nu$	4
External photo-processes[a]	$C_3N + h\nu \rightarrow C_2 + CN$	175
Internal photo-processes[a]	$CO + h\nu \rightarrow C + O$	192

[a] External photo-processes are those induced by the interstellar radiation field; internal photo-processes are induced by radiation generated in dark clouds by the interaction of molecules, especially H_2, with cosmic rays. Further details and examples are given in Section 4.5.

Smith (2011)

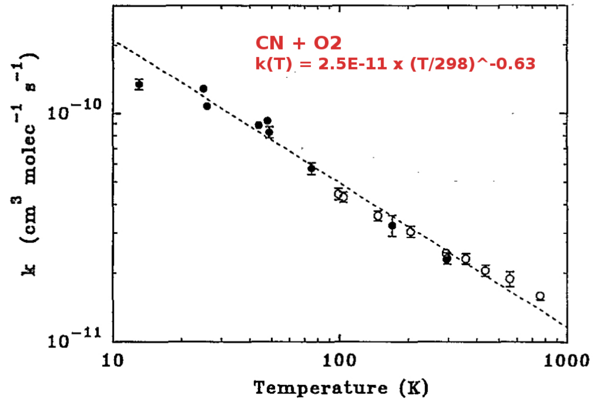
Barrierless reactions





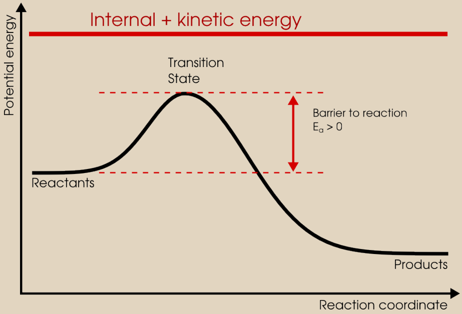
- radical-radical reaction (e.g. $CN + O_2$)
- $k(T) = \alpha(T/300)^\beta$, $\approx 10^{-10}\,\mathrm{cm^3\,s^{-1}}$ at 10 K

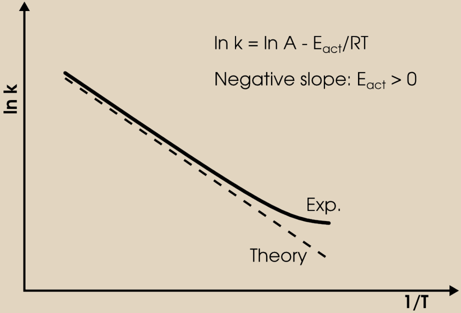
Example: CN + O_2



Sims I. R. et al, J Chem Phys 1994

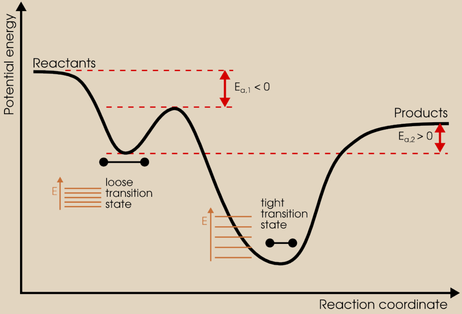
Arrhenius-type reactions

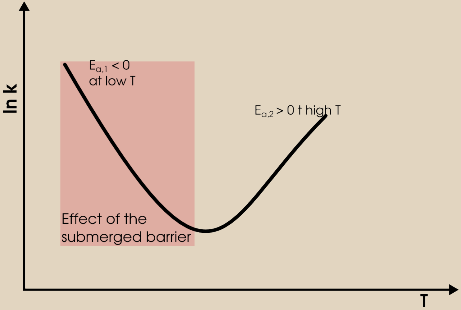




- neutral-neutral reaction
- $k(T) = A\exp(-E_a/T)$, $\approx 10^{-11}\ \mathrm{cm^3\,s^{-1}}$ at 10 K
- A $(\mathrm{cm^3\,s^{-1}})$: pre-exponential factor; rate of collisions
- E_a (K): activation energy
- $\exp(-E_a/T)$: fraction of colliders with kinetic energy larger than E_a (M-B distrib.)

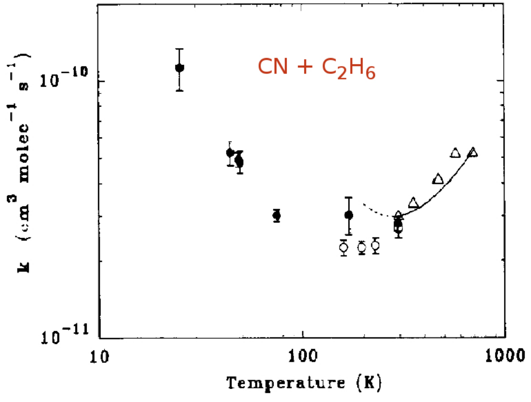
Special case: submerged barrier





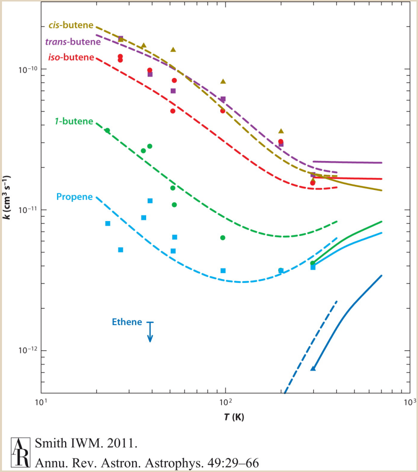
- rate increases at low-T up to $10^{-10}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$
- observed in many neutral-neutral reactions involving radicals and unsaturated species
- must be fast at 300 K
- was evidenced using CRESU method (France/Rennes)

Example: CN + C_2H_6



Sims I. R. et al, Chem Phys Let 1993

Fast n-n at low-T



Smith (2011)

Reactions with atomic oxygen

Types of reactions and orders of magnitude

Type	Example	$k(T)$
CR ionization	$\mathrm{He} + \mathrm{CRP} \longrightarrow \mathrm{He}^+ + \mathrm{e}^-$	10^{-16}–$10^{-17}\,\mathrm{s}^{-1}$
ion-neutral	$\mathrm{CO} + \mathrm{H}_3^+ \longrightarrow \mathrm{HCO}^+ + \mathrm{H}_2$	$10^{-9}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$
neutral-neutral	$\mathrm{N} + \mathrm{CH} \longrightarrow \mathrm{CN} + \mathrm{H}$	$10^{-11}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$
Charge exchange	$\mathrm{O}^+ + \mathrm{H} \longrightarrow \mathrm{O} + \mathrm{H}^+$	$10^{-10}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$
Dissociative recombination	$\mathrm{NH}_4^+ + \mathrm{e}^- \longrightarrow \mathrm{NH}_3 + \mathrm{H}$	$10^{-6}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$
Radiative recombination	$\mathrm{C}^+ + \mathrm{e}^- \longrightarrow \mathrm{C} + h\nu$	$10^{-12}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$
Radiative association	$\mathrm{C}^+ + \mathrm{H}_2 \longrightarrow \mathrm{CH}_2^+ + h\nu$	$10^{-17}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$
Photoionization	$\mathrm{C} + h\nu \longrightarrow \mathrm{C}^+ + \mathrm{H}$	$10^{-9}\,\exp(-\gamma A_\mathrm{V})\,\mathrm{cm}^3\,\mathrm{s}^{-1}$
Photodissociation	$\mathrm{H}_2\mathrm{O} + h\nu \longrightarrow \mathrm{OH} + \mathrm{H}$	$10^{-9}\,\exp(-\gamma A_\mathrm{V})\,\mathrm{cm}^3\,\mathrm{s}^{-1}$

- Kinetic rate coefficients are usually written as:

$$k(T) = \alpha\,(T/300)^\beta\;\exp(-\gamma/T)\;\mathrm{cm}^3\,\mathrm{s}^{-1}$$

- Modified Arrhenius form
- $\gamma \sim \Delta G$, or $\gamma \sim E_a$

Gas-phase chemistry: typical sequence

1. Chemistry starts with ions
   - $H_2 + CRP \longrightarrow H_2^+ + e^-$ (85% of the time)
   - $He + CRP \longrightarrow He^+ + e^-$
   - He^+ will ionize/dissociate almost anything
2. Ions then collide primarily with H and H_2
   - $H_2 + H_2^+ \longrightarrow H_3^+$: small proton affinity, universal proton donnor
   - $X + H_3^+ \longrightarrow XH^+ + H_2$
3. *Hydrogen abstractions*: $XH^+ + H_2 \longrightarrow XH_2^+ + H$, etc
   - until saturation: NH_4^+, CH_5^+, H_3O^+
4. *Dissociative recombinations*: $XH_n^+ + e^- \longrightarrow XH_{n\text{-}1} + H$
   - Example: H_2O, NH_3, HCO^+, CHn
   - Difficulty: branching ratios of output channels

Kinetic rate coefficients

$$k(T)\ ?$$

Theoretical calculations of kinetic coefficients

Non-reactive collisions

- Born-Oppenheimer approximation
- Potential energy surface (PES) down to $\sim$10 K precision
- PES-fitting
- Dynamics on the PES
- Averaging over Maxwell-Boltzmann velocity distribution

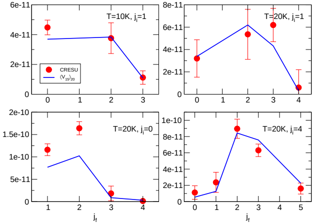
Reactive collisions

- B-O approximation
- Compute energetics for different approaching 3D geometry
- Search for extrema (minimum, saddle points)
- Compute dynamics along this path

Measurements of kinetic coefficients

- Laboratory experiments: down to 50 K (e.g. Bordeaux) + numerical extrapolations downwards; 5 K (Rennes)
- Different techniques: usually, measure the disappearance of reactants (w/o disentangling among products)
- General reference: Smith (2011)

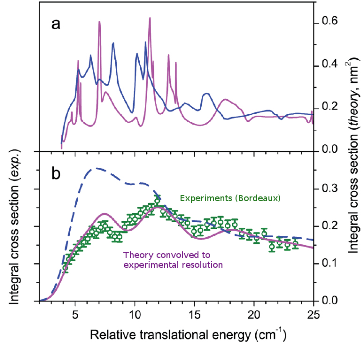
Experiments vs theory: non-reactive systems



- Absolute agreement between theory and experiments; Sims, Faure et al (Rennes/Grenoble collab.)

- Validation of theory and experiments is obtained jointly
- Non-reactive systems first
- reactive systems so far limited to 3 atoms (e.g. $F + H_2 \longrightarrow HF + H$)

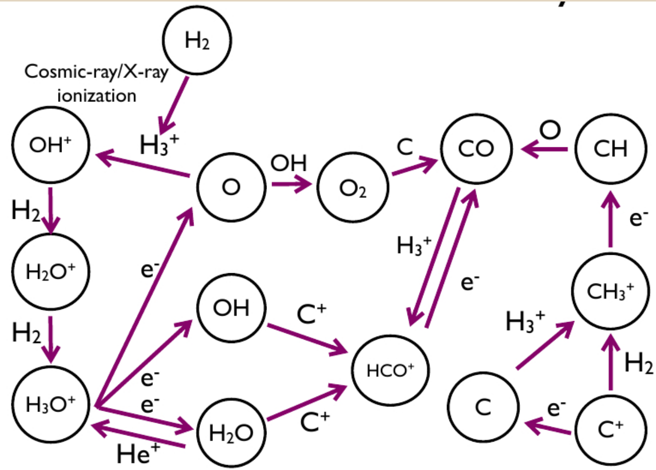
Experiments vs theory: non-reactive systems



- Absolute agreement between theory and experiments; Sims, Faure et al (Rennes/Grenoble collab.)
- Quantum resonances in CO-H_2 inelastic collisions; Costes & Naulin 2016

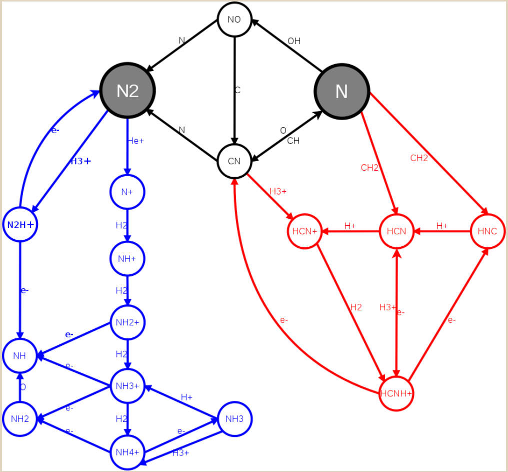
- Validation of theory and experiments is obtained jointly
- Non-reactive systems first
- reactive systems so far limited to 3 atoms (e.g. $\mathsf{F} + \mathsf{H}_2 \longrightarrow \mathsf{HF} + \mathsf{H}$)

Gas-phase chemical networks



From E. Bergin

Gas-phase chemical networks



Hily-Blant et al. (2013); Le Gal et al. (2014)

Networks

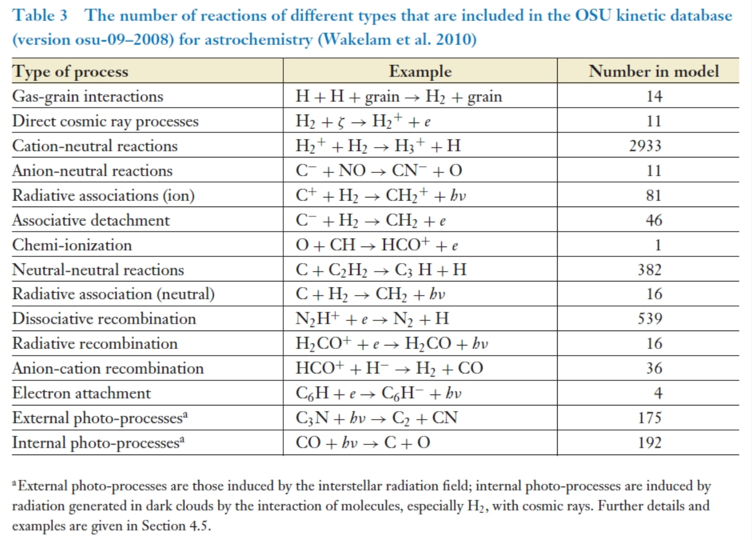


Table 3 The number of reactions of different types that are included in the OSU kinetic database (version osu-09–2008) for astrochemistry (Wakelam et al. 2010)

Type of process	Example	Number in model
Gas-grain interactions	$H + H + \text{grain} \rightarrow H_2 + \text{grain}$	14
Direct cosmic ray processes	$H_2 + \zeta \rightarrow H_2^+ + e$	11
Cation-neutral reactions	$H_2^+ + H_2 \rightarrow H_3^+ + H$	2933
Anion-neutral reactions	$C^- + NO \rightarrow CN^- + O$	11
Radiative associations (ion)	$C^+ + H_2 \rightarrow CH_2^+ + h\nu$	81
Associative detachment	$C^- + H_2 \rightarrow CH_2 + e$	46
Chemi-ionization	$O + CH \rightarrow HCO^+ + e$	1
Neutral-neutral reactions	$C + C_2H_2 \rightarrow C_3H + H$	382
Radiative association (neutral)	$C + H_2 \rightarrow CH_2 + h\nu$	16
Dissociative recombination	$N_2H^+ + e \rightarrow N_2 + H$	539
Radiative recombination	$H_2CO^+ + e \rightarrow H_2CO + h\nu$	16
Anion-cation recombination	$HCO^+ + H^- \rightarrow H_2 + CO$	36
Electron attachment	$C_6H + e \rightarrow C_6H^- + h\nu$	4
External photo-processes[a]	$C_3N + h\nu \rightarrow C_2 + CN$	175
Internal photo-processes[a]	$CO + h\nu \rightarrow C + O$	192

[a] External photo-processes are those induced by the interstellar radiation field; internal photo-processes are induced by radiation generated in dark clouds by the interaction of molecules, especially H_2, with cosmic rays. Further details and examples are given in Section 4.5.

k_L ($\times 10^{-9}$ cm^3 s^{-1})

$\sim 10^{-9}$

$\sim 10^{-11}$ up to 10^{-10}

$\sim 10^{-7}\, T^{a}$, ^{a}=0.5-1

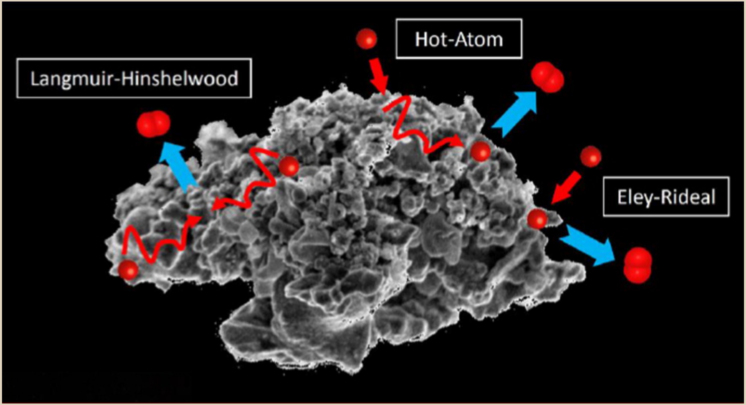
I- The building blocks

1. Introduction & Outline
2. Abundances
3. Interstellar chemistry: general characteristics
4. Gas-phase chemistry
5. Surface chemistry (1)
6. Summary

The limits of gas-phase processes

- Formation of H_2 in the present-day universe: too slow (2-body radiative association, three-body)
- formation of water in prestellar cores and protostars (van Dishoeck 2014)
- methanol
- aceto-nitrile NH_2CH_2CN (Belloche et al. 2008), precursor of glycine amino-acid ?

Surface chemistry: the formation of H_2



Linnartz et al. (2015)

Usual description: H atoms adsorb on the surface, migrate (tunnelling, thermal hopping), encounter and form a H_2 molecule, liberating 4.5 eV, evenly distributed among phonon, kinetic, and internal energy.

Surface chemistry: the formation of H_2

- Formation of H_2 on grains: pseudo one-order kinetics

$$\frac{dn(\mathrm{H}_2)}{dt} = Rn(\mathrm{H})n_\mathrm{H}$$

- In the above: $n_\mathrm{H} \propto n_g$; $R \approx 2-3\times10^{-17}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ (Jura 1975)
- Fully molecular gas requires H_2 self-shielding
- S: sticking probability; ϵ: probability of reaction upon encounter; a: average dust size;
- $R = 1/2\epsilon S\Sigma_g v_\mathrm{th} n(\mathrm{H})$

Surface of dust

- First parameter from astrochemical point of view: total grain surface per unit volume
- formation of H_2, chemistry, UV extinction, thermal balance
- For MRN-like size distribution ($n(a) \propto a^{-3.5}$), surface in small grains (mass in large grains): coagulation decreases surface available for chemistry (and extinction, and photoelectric effect with secondary photons, hence charge, etc !)
- Grain growth in disks (see Dartois and Dutrey lectures)

Interrupted here: continuation in Lecture 2

I- The building blocks

Summary for today

- Chemistry is not an option
- Chemistry is a serious field of research in astrophysics
- Time-dependent calculations depend on the initial conditions
- Set of elemental abundances is a fundamental problem
- Understand gas-phase processes in the pre-stellar phase to determine the initial conditions of protoplanetary disks
- My opinion: grain-surface chemistry is an experimentally- and observationally-driven field

End of Part 1

Tomorrow: 8:30 am

To which extent is the product of the pre-stellar chemistry preserved in primitive planetary systems ?