CH_4-CH_3-C_2H_6 IN TITAN'S ATMOSPHERE: EXPLICIT SOLUTIONS AND NEAR-STEADY STATE OF A SIMPLIFIED REACTION SYSTEM.

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Introduction: Methane gas (CH_4) is one of the main components of the atmosphere of Titan, the largest satellite of Saturn. At present, pCH_4 = 0.1 bar, and the remainder made of N_2 at the total P = 1.5 bar. Methane undergoes thermal escape from Titan's atmosphere and photolytic dissociation to other hydrocarbons [2, 3]. The very detailed sequence of reactions leading from CH_4 to CH_3 to ethane C2H6 accumulating on Titan's surface and other produtcs may be replaced by a simplified system of three reactions [1]:

(1) $d[CH_4]/dt = - k_{12}[CH_4]$ k_{12} (yr^{r-1})

(2) $d[CH_3]/dt = k_{12}[CH_4] - k_{23}[CH_3]^2$ k_{23} (cm^3 molec^{-1} yr^{-1})

(3) $d[C_2H_6]/dt = k_{23}[CH_3]^2 - k_3[C_2H_6]$ k_3 (yr^{-1})

where brackets [ ] denote concentrarions in molecules/cm^3.

Eqs. (1) and (3) are first-order ordinary differentiasl equations (ODE), and (2) is a Riccati equation. Eqs. (1)-(3) can be solved numerically for known values of the reaction rate pasrameters k_i, but no explicit solution, as far as we are aware, has been published for the tnire reaction system.

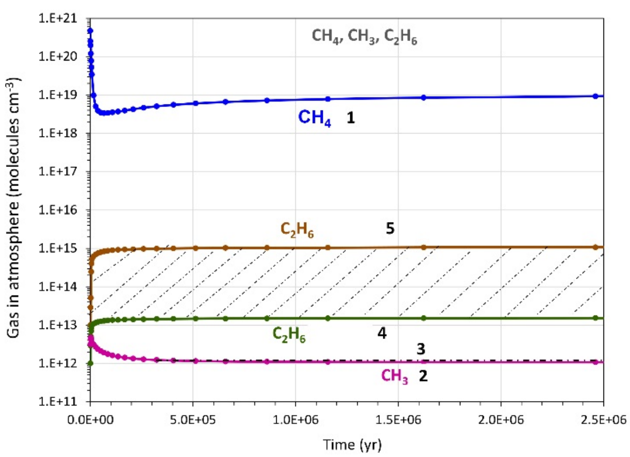

Fig. 1. Calculated concentrations of CH_4, CH_3, and C_2H_6 in Titan's atmosphere. **1:** CH_4 [2]. **2:** CH_3 concentration from eq. (2), $k_{12} = 6.7\times10^{-9}$ yr^{-1}, $k_{23} = 5\times10^{-14}$ cm^3 molecule^{-1} yr^{-1}. **3:** CH_3 from eq. (2b), rate parameters as in **2**. **4:** C_2H_6 from eq. (5), $k_{23} = 1\times10^{-12}$ cm^3 molecule^{-1} yr^{-1}, $k_3 = 5\times10^{-3}$ yr^{-1}. **5:** C_2H_6 from eq. (5), $k_{23} = 1\times10^{-12}$ cm^3 molecule^{-1} yr^{-1}, $k_3 = 1\times10^{-3}$ yr^{-1}. Cross-hatched area is the domain of C_2H_6 reported concentrations.

Solution of (1), on next page:

Reaction Rate Parameters k_i: From the very extensive data base of experimentally and theoretically determined values of k_{12}, k_{23}, and k_3, their ranges are: k_{12} from 9.5E-09 to 3E-04 yr^{-1}; k_{23} from 5.1E-19 to 1.3E-03 cm^3 molecule^{-1} yr^{-1}; k_3 from 1.3E-80 to 3E+0 yr^{-1}. The ranges are very large and values $<1.5\times10^{-10}$ yr^{-1} correspond to reaction half-lives longer than the age of the Solar system, 4.55×10^9yr. The rate constants cannot be chosen arbitrarily to make the equations produce present-day concentrations of CH_4, CH_3, and C_2H_6 in Titan's atmosphere. The value that agree with the present day concentrations (Fig. 1) are k_{12} = 6.7E-09 yr^{-1}, k_{23} = 5E-14 to 1E-12 cm^3 molecule^{-1} yr^{-1}, and $k3$ = 1E-04 to 1E-03 yr^{-1}.

Present-Day Abundance: Present day abundances of CH_4, CH_3, and C_2H_6 in Titan's atmosphere are given in Table 1.

Table 1. Gas abundances in Recent Titan's atmosphere

Gas	Abundance		References
	molecules cm^{-3}	**kg**	
CH_4	1.31×10^{19}	6.16×10^{17}	[4], [5], [6], [2]
CH_3	1.05×10^{12}	4.62×10^{10}	[7]
C_2H_6	1.81×10^{13}– 1.67×10^{15}	1.60×10^{12}– 1.48×10^{14}	[8], [9], [7]. [10]
Mean	8.46×10^{14}		
Geom.	1.74×10^{14}		

Near-Steady-State Concentrations: In the course of Titan's cooling since accretion, thermal escape of CH_4 slowed down, approaching the present-day atmospheric mass [2]. This suggests that at the present temperature of about 94 K, Titan's atmosphere has attained a near-steady state. The steady state or asymptotic solutions of eqs. (1)-(3) and (2a)-(3a) give the same results [11]:

From (2), (2a), (2b),

$$(4)\quad [CH_3]_{ss} = \sqrt{\frac{k_{12}[CH_4]_{ss}}{k_{23}}}$$

From (3), (3a),

$$(5)\quad [C_2H_6]_{ss} = \frac{k_{23}[CH_3]_{ss}^2}{k_3} = \frac{k_{12}[CH_4]_{ss}}{k_3}$$

The computed concentrations from the preceding two equations and k_i values cited above are given in Table 2.

(1a) $[\mathrm{CH_4}] = [\mathrm{CH_4}]_{ss} + ([\mathrm{CH_4}]_0 - [\mathrm{CH_4}]_{ss})e^{-k_{12}t}$

where $[CH_4]_0$ is the initial and $[CH_4]_{ss}$ steady-stater concentration (Fig. 1)

Solution of (2), from [11]:

$$\frac{d[\mathrm{CH_3}]}{dt} = k_{12}[\mathrm{CH_4}]_{\mathrm{ss}} + (k_{12}[\mathrm{CH_4}]_0 - k_{12}[\mathrm{CH_4}]_{\mathrm{ss}})e^{-k_{12}t} - k_{23}[\mathrm{CH_3}]^2$$

(2a) $$[\mathrm{CH_3}] = -\frac{1}{k_{23}}\frac{(pCk_{12}/2)e^{-k_{12}t/2}\, I'_\nu\left(Ce^{-\lambda t/2}\right)(qC\lambda/2)e^{-\lambda t/2}\, I'_{-\nu}\left(Ce^{-\lambda t/2}\right)}{pI_\nu(Ce^{-\lambda t/2}) + qI_{-\nu}(Ce^{-\lambda t/2})}$$

where *C* and *ν* are constants defined in terms of k_i, $[CH_4]_0$, $[CH_4]_{ss}$, and constants $q = 1$, $p = -1$.

Alternatively, in the regime where the CH_4 concentrration is near steady-state, $[CH_4]_{ss}$, after ~5×10^5 yr (Fig. 1),

$$\frac{d[\mathrm{CH_3}]}{dt} = k_{12}[\mathrm{CH_4}]_{ss} - k_{23}[\mathrm{CH_3}]^2$$

(2b) $[\mathrm{CH}]_3 = \sqrt{\frac{k_{12}[\mathrm{CH_4}]_{\mathrm{ss}}}{k_{23}}}\tanh(\sqrt{k_{12}[\mathrm{CH_4}]_{ss}k_{23}}\,t)$, and substituting the latter in (3), we have

$$\frac{d[\mathrm{C_6H_6}]}{dt} = k_{12}[\mathrm{CH_4}]_{\mathrm{ss}}\tanh^2(\sqrt{k_{12}[\mathrm{CH_4}]_{ss}k_{23}}\,t) - k_3[\mathrm{C_6H_6}]$$

(3a) The solution of the preceding equation is, finally, $[C_2H_6] = f(t) + \mathrm{CONST}\times\exp(-k_3t)$

$$f(t) = \frac{k_{12}[\mathrm{CH_4}]_{\mathrm{ss}}}{ac(a+2c)}\left[a^2e^{2ct}\,\boldsymbol{F}\left(1,\frac{a}{2c}+1;\ \frac{a}{2c}+2;\ -e^{2ct}\right) - (a+2c)\left(a\,\boldsymbol{F}\left(1,\frac{a}{2c};\ \frac{a}{2c}+1;\ -e^{2ct}\right) + a\tanh(ct) - c\right)\right]$$

where $a = k_3$ yr^{-1}; and $c = (k_{12}\cdot[CH_4]_{ss}\cdot k_{23})^{0.5}$ yr^{-1}, and ***F*** or Gauss's function ${}_2\boldsymbol{F}_1$ is the hypergeometric series.

And: CONST = – *f(t* = 0*)*.

Table 2. Calculated and reported CH_4, CH_3, and C_2H_6 concentrations in present-day Titan's atmosphere.

Fig. 1	Rate parameter	Value	CH_4 (molecule/cm^3)		CH_3 (molecules/cm^3)		C_2H_6 (molecules/cm^3)	
			Calc.	Rep.	Calc.	Rep	Calc.	Rep.
1. CH_4	*k* escape k_{12} $\times[CH_4]_{ss}$	Variable [2] 8.76×10^{10}	1.31×10^{19}	1.31×10^{19}				
2. CH_3 eq. (2)	k_{12} k_{23}	6.7×10^{-9} 5.0×10^{-14}			1.35×10^{12}	1.15×10^{12}		
3. CH_3 eq. (2b)	k_{12} k_{23}	6.7×10^{-9} 5.0×10^{-14}			0.94×10^{12}			
4. C_2H_6	k_{23} k_3	1.0×10^{-13} 1.0×10^{-3}					1.3×10^{13}	1.81×10^{13} to 1.67×10^{15}
5. C_2H_6	k_{23} k_3	1.0×10^{-12} 1.0×10^{-4}					1.3×10^{15}	

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