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Global Thermodynamic Atmospheric Modeling: Search for New Heterogeneous Reactions

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This article demonstrates quantitatively how far reactions are from chemical equilibrium over the full space of a two-dimensional atmospheric model. This method could be used with data where an instrument-equipped aircraft measures numerous species simultaneously. An atmospheric reaction is displaced from equilibrium by solar radiation and relocation of species by atmospheric motions. One purpose of this study is to seek additional stratospheric or tropospheric gas-phase chemical reactions that might undergo heterogeneous catalysis. Hypothetical cases can be rapidly screened in terms of their thermodynamic potential to react under measured or modeled atmospheric conditions of temperature and local species concentrations. If a reaction is interesting, is slow in the gas phase, and has a high thermodynamic tendency to react, it is a good candidate for a laboratory study to seek a heterogeneous catalyst. If the reaction is thermodynamically unfavorable, there is no catalyst that can cause the reaction to occur. If a reaction is thermodynamically favored to occur but also endothermic, it will tend to be slow at stratospheric temperatures. We find, as expected, that four heterogeneous reactions important in causing the Antarctic "ozone hole" have high thermodynamic tendencies to occur under atmospheric conditions, but one of these is only weakly thermodynamically allowed in some regions of the atmosphere. The reaction of SO_2 and HNO_3 to form HONO has a high thermodynamic potential to occur, is a well-known laboratory reaction at ice temperature, and may occur in nitric acid-rich sulfate aerosols. Throughout the troposphere and stratosphere, we find that formaldehyde has an extremely high thermodynamic potential to reduce nitric acid. Formaldehyde is known to stick to and remain in sulfuric acid solution, where it adds water to form $H_2C(OH)_2$. Near room-temperature $H_2C(OH)_2$ reacts with nitric acid in a two-step mechanism to form two molecules of HONO, but the rate of this process under conditions of stratospheric sulfuric acid aerosols is unknown.

Introduction

In this paper we present a method, an extension of the (K/Q) method of Burley and Johnston,[1] for identifying the thermodynamic feasibility of gas-phase reactions to undergo heterogeneous catalysis in the atmosphere. Our analysis is limited by the available concentration data in the Lawrence Livermore National Laboratory (LLNL) model, which extends from pole to pole and altitudes of 0 to 60 km, and by accessible thermodynamic data for atmospheric species.[2] Seasonal and daytime effects are assessed using the LLNL model concentrations at midnight and noon both in June and September. In most cases, we examine gaseous reactants and products to find the degree to which thermodynamics favors or forbids the overall reaction to occur. If a reaction is thermodynamically favorable but does not occur in the gas phase, it is reasonable to inquire whether it might be made to occur by way of heterogeneous catalysis. If a reaction is thermodynamically unfavorable, no catalyst can cause it to proceed from reactants to products, although it can be driven by photochemistry. The procedure outlined in this paper does not consider the chemical thermodynamics or physics of the processes that occur between gas-phase and condensed-phase species or inside the condensed phase (see Molina et al., 1996).[3]

Methodology

The derivation is straightforward,[4] but it is presented here for the definition of terms and as a point of reference. The chemical potential of a substance, μ, is a fundamental property derived from the laws of thermodynamics and observed physical properties, and it represents the criterion for chemical equilibrium and the direction for spontaneous change. Chemical potential, μ, decreases when a substance undergoes spontaneous change, remains the same for small perturbations about equilibrium, and increases when reversible work is applied.[4] Since this article is concerned primarily with gases at low concentrations in the atmosphere, we use the ideal-gas approximation throughout. The derivation starts with the statement "The chemical potential of a substance A in any actual state, μ_A, is the chemical potential of A in its defined standard state, $\mu_A°$, plus the change in chemical potential in going from the standard state to the actual state." For an ideal gas the change of chemical potential per mole in going from its standard partial pressure $p°$ to its actual partial pressure p is given by $RT \ln(p/p°)$. This leads to the following equation:

$$\mu_A = \mu_A° + RT \ln(p/p°) \qquad (1)$$

where the value of $\mu_A°$ depends on the standard state, which is usually 1 atm or 1 bar in tables of thermodynamic data.

Consider the balanced chemical equation of the general form

$$xA + yB = zC + wD \qquad (2)$$

where A, B, C, and D are four ideal gases mixed in any amounts and *x*, *y*, *z*, and *w* are the stoichiometric integers required to balance the equation. With each reactant and product expressed in the form shown in eq 1, the difference in chemical potential between the standard state and actual state is

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$$\Delta_r\mu = z\mu_C + w\mu_D - x\mu_A - y\mu_B \tag{3}$$

$$= \Delta_r\mu^\circ + RT \ln \frac{[p_C{}^z p_D{}^w/(p_A{}^x p_B{}^y)]_{\mathrm{ACTUAL}}}{[p_C{}^z p_D{}^w/(p_A{}^x p_B{}^y)]_{\mathrm{STANDARD}}}$$

Since p° is equal to one standard state unit, $p/p^\circ = p/1 = p$, eq 3 can be simplified, where each pressure is implicitly a dimensionless quantity:

$$\Delta_r\mu = \Delta_r\mu^\circ + RT \ln\left(\frac{p_C{}^z p_D{}^w}{p_A{}^x p_B{}^y}\right)_{\mathrm{ACTUAL}} \tag{4}$$

$$= \Delta_r\mu^\circ + RT \ln Q(p)$$

where Q is defined as

$$Q(p) = \left(\frac{p_C{}^z p_D{}^w}{p_A{}^x p_B{}^y}\right)_{\mathrm{ACTUAL}} \tag{5}$$

The term p (actual) refers to the measured or modeled pressure (LLNL model in this article) of each species at specified altitude, latitude, season, and time of day. The chemical equilibrium constant, K, is defined as

$$K(p) = \left(\frac{p_C{}^z p_D{}^w}{p_A{}^x p_B{}^y}\right)_{\mathrm{EQUIL}} \tag{6}$$

At chemical equilibrium, the chemical potential of the reactants equals the chemical potential of the products, that is, $\Delta_r\mu = 0$. The pressures of reactants and products are at chemical equilibrium values. Consequently, $K = Q_{\mathrm{EQUIL}}$. By substituting $\Delta_r\mu = 0$ and $K = Q_{\mathrm{EQUIL}}$ into eq 4, we obtain for chemical equilibrium

$$\Delta_r\mu^\circ = -RT \ln K \tag{7}$$

Substituting eqs 5 and 7 into eq 4, we obtain the fundamental expression for measuring the distance. An actual reaction is from the chemical equilibrium state

$$\frac{-\Delta_r\mu}{RT} = \ln \frac{K}{Q} \tag{8}$$

A reaction is thermodynamically favored to go from reactants to products if $\Delta_r\mu < 0$. It is thermodynamically favored to go from products to reactants if $\Delta_r\mu > 0$. When $\Delta_r\mu = 0$, the reaction is at chemical equilibrium. In the context of eq 2 this corresponds to the following.

$$\text{If } K/Q > 1 \text{ or } \log(K/Q) > 0,\ A + B \rightarrow C + D \tag{9}$$

$$\text{If } K/Q < 1 \text{ or } \log(K/Q) < 0,\ A + B \leftarrow C + D$$

$$\text{If } K/Q = 1 \text{ or } \log(K/Q) = 0,\quad A + B \text{ are in chemical equilibrium with } C + D$$

If log (K/Q) is between about -1 to $+\,1$, the actual reactants and products are close to chemical equilibrium. The expression $\log(K/Q)$ is a quantitative indicator with continuous gradations of the thermodynamic potential for a reaction to proceed from reactants to products.

In chemical thermodynamics, the "reaction of formation" of a substance A from its component elements, E_1, E_2, E_3, ..., each in its standard state, is

$$\{\alpha E_1 + \beta E_2 + \gamma E_3 + ... = A\}^\circ \quad \text{in general} \tag{10}$$

$$\{(1/2)H_2 + 2O_2 + (1/2)N_2 = HOONO_2\}^\circ \quad \text{for example}$$

where α, β, γ are integers or ratios of integers. The equilibrium constant for the reaction of formation, K_f, is

$$K_f(A) = \left[\frac{p(A)}{p(E_1)^\alpha p(E_2)^\beta p(E_3)^\gamma}\right]_{\mathrm{EQUIL}} \tag{11}$$

Thermodynamic values of log K_f are tabulated as the last column of data in the JANAF tables[2] for a wide range of atmospheric species and temperatures, including 200 and 300 K, which encompass almost the total range of atmospheric temperatures in this study. For the general reaction 2, the equilibrium constant (eq 6) is related to K_f by

$$\log K = z \log K_f(C) + w \log K_f(D) - x \log K_f(A) - y \log K_f(B) \tag{12}$$

In general, an equilibrium constant is a function of temperature. To determine log $K(T)$ values at temperatures between 190 and 300 K, we adopt the standard linear variation of log $K(T)$ with respect to $1/T$ and apply the following relationship:

$$\log K(T) = \log K(200) + [(\log K(300) - \log K(200))][(200^{-1} - T^{-1})/(200^{-1} - 300^{-1})] \tag{13}$$

This approximation has been checked for reactions considered in this study for which formation constants at 250 K are given in ref 2. Errors in log K_f values at 250 K are negligible, being between -0.02 to $+\,0.01$.

To ensure that K/Q is dimensionless, it is essential for K (from tables of thermodynamic data) and Q (observed or modeled) to have the same standard state, that is, be expressed in the same units. In the LLNL model and in our study, the standard state for gases is concentration $c(A)^\circ = [A]^\circ = 1$ molecule cm^{-3}. K_f values from the JANAF tables[2] are quoted with a standard state of 1 bar. Starting with $pV = nRT$, we find $c = 7.24274 \times 10^{21} p/T$, where p is expressed in bars and the following conversion is necessary:

$$\log(K/\text{molecules cm}^{-3}) = \log(K/\text{bar}) + \Delta_r n(21.860 - \log T) \tag{14}$$

$$\Delta_r n = z + w - x - y \tag{15}$$

In situations where the concentrations of all relevant species are known, we use this procedure to prepare two-dimensional contour plots of $\log(K/Q)$ as a function of altitude (y) and latitude (x). At a glance, these contour plots show the extent of a reaction's displacement from chemical equilibrium at all latitudes and altitudes.

The equilibrium constant at one temperature can be expressed in terms of the change of enthalpy $\Delta_r H^\circ$ ("heat of reaction") and change of entropy $\Delta_r S^\circ$:

$$\ln K = -\frac{\Delta_r H^\circ - T\Delta_r S^\circ}{RT} = -\frac{\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R} \tag{16}$$

A large value of the equilibrium constant is favored by a negative change of enthalpy (exothermic reaction) and a positive change of entropy as reaction occurs. The change in enthalpy in going from reactants to products, $\Delta_r H^\circ$, averaged between 200 and 300 K, is

$$\Delta_r H^\circ/\text{kJ mol}^{-1} = \frac{2.303R}{1000}\,\frac{[\log K(300) - \log K(200)]}{[1/200 - 1/300]} \qquad (17)$$

A major factor in determining the change in entropy for a given reaction is the change in number of gas molecules as reactants go to products, $\Delta_r n$ (eq 15). If a reaction is endothermic, $\Delta_r H^\circ > 0$, there is a general, useful relation between thermodynamics and chemical kinetics: the kinetic activation energy E must be equal to or greater than $\Delta_r H^\circ$, where activation energy is defined as E in the Arrhenius rate constant expression

$$k = A\,\mathrm{e}^{-E/(RT)} \qquad (18)$$

A reaction, which is thermodynamically favored by an increase of entropy ($\Delta_r n > 0$), may be kinetically limited by an activation energy inferred from a positive $\Delta_r H^\circ$.

Results with *K/Q* Method

Chemical reactions discussed here are identified by a number and the symbol #, and a single sequence of reactions numbered #1−#33 runs through Tables 1−3. Results of log(K/Q) are summarized in Table 1. For each of 14 reactions, the range of log(K/Q) over the two-dimensional atmospheric model is given for (i) September 21 noon, (ii) September 21 midnight, (iii) June 21 noon, and (iv) June 21 midnight. For each reaction there is a brief comment concerning whether thermodynamics favors the occurrence of the reaction, does not allow it to occur, or gives a mixed result depending on altitude, latitude, time of day, or season. Negative heat of reaction, $-\Delta_r H^\circ$ (eq 17), and increase of gas volume upon reaction, $\Delta_r n$ (eq 15), are listed in Tables 1 and 3.

Difference between Chemical Equilibrium and Photochemical Steady State. We carried out this procedure for a case that is fundamental to atmospheric chemistry, the balance between ozone and molecular oxygen (Chapman,[5] 1930):

$$2O_3 = 3O_2 \qquad (\#1)$$

The convention in all latitude−altitude plots is that −90, 0, and 90 latitudes correspond to the south pole, equator, and north pole, respectively. Figure 1 shows values of log(K/Q) for #1 at all latitudes, altitudes 0−60 km, June, noon. We made similar plots at June midnight, September noon, and September midnight, and the four plots are so nearly alike that it is pointless to show more than one. Ozone is thermodynamically unstable with respect to oxygen. Reaction #1, $2O_3 = 3O_2$, is 286 kJ mol $^{-1}$ exothermic (eq 17), and it occurs with a 50% increase in number of gas molecules (eq 15). Since the concentration of molecular oxygen is about a million-fold larger than that of ozone, the concentration of oxygen is essentially constant as ozone reacts according to reaction #1, and the actual and equilibrium concentrations of O_2 are essentially equal. Consequently, K/Q is equal to $([O_3]_{\text{ACTUAL}}/[O_3]_{\text{EQUIL}})^2$ and thus

$$[O_3]_{\text{ACTUAL}}/[O_3]_{\text{EQUIL}} = (K/Q)^{1/2} \qquad (19)$$

$$\log([O_3]_{\text{ACTUAL}}/[O_3]_{\text{EQUIL}}) = (1/2)\log(K/Q)$$

The actual concentration of ozone in the troposphere and stratosphere exceeds the equilibrium concentration by 23−40 orders of magnitude (Figure 1 and eq 19).

There is a difference between “chemical equilibrium” and “photochemical steady state”, which is sometimes called “photochemical equilibrium”. Chemical equilibrium is the dynamic balance between reactants and products with no external source of energy. Every molecular process is balanced by its exact reverse, and both proceed at the same rate, on average, at chemical equilibrium. In the Chapman mechanism for oxygen chemistry, photochemical steady state for reaction #1 is obtained by the pumping action of two photochemical reactions and two thermal chemical reactions:

$$j_1\text{:}\quad O_2 + h\nu\ (\text{l} < 242\ \text{nm}) = O + O \quad \text{slow}$$

$$k_1\text{:}\quad O + O_2 + M = O_3 + M \quad \text{fast}$$

$$j_2\text{:}\quad O_3 + h\nu\ (\text{vis and UV}) = O_2 + O \quad \text{fast}$$

$$k_2\text{:}\ O + O_3 = 2O_2 \quad \text{slow}$$

which sets up a steady-state concentration of atomic oxygen and of ozone:

$$[O]_{\text{PHOTO STEADY STATE}} = \frac{j_2[O_3]}{k_1[M][O_2]}$$

$$[O_3]_{\text{PHOTO STEADY STATE}} = \left(\frac{j_1 k_1[M]}{j_2 k_2}\right)^{1/2}[O_2]$$

This photochemical steady-state concentration of ozone by the Chapman mechanism exceeds the chemical thermodynamic equilibrium concentration by many orders of magnitude, comparable to those in Figure 1 and Table 1 (reaction #1). Ozone is never at chemical equilibrium in the atmosphere.

Also, ozone undergoes thermal decomposition:

$$k_3\text{:}\quad O_3 + M = O_2 + O + M$$

However, the thermal decomposition of ozone is so slow as to be negligible at tropospheric and stratospheric temperatures, but the rate becomes very fast as the temperature rises above 100 °C.

Within the Chapman mechanism, the conversion of ozone to oxygen is strongly thermodynamically favored, and the rate of this conversion is slow. By satisfying these two conditions, reaction #1 satisfies the necessary condition for being sped up by catalysis; the sufficient condition is to find a suitable catalyst. Indeed, the decomposition of ozone is well-known to be catalyzed by free radical pairs (OH/HOO,[6] NO/NO_2,[7,8] Cl/ClO,[9,10] and others) through homogeneous gas-phase catalytic cycles, illustrated below with two examples:

$$OH + O_3 = HOO + O_2$$

$$HOO + O_3 = OH + 2O_2$$

$$\text{net:}\quad 2O_3 = 3O_2 \qquad (21a)$$

$$NO + O_3 = NO_2 + O_2$$

$$NO_2 + O = NO + O_2$$

$$\text{net:}\quad O_3 + O = 2O_2 \qquad (21b)$$

Two Illustrative Reactions in Table 1. Smith[11] [1947] observed reaction #2 to occur between 330 and 273K:

$$NO + 2HNO_3 = 3NO_2 + H_2O \quad \text{all gases} \qquad (\#2)$$

The results were interpreted, in part, on the basis of surface adsorption and heterogeneous catalysis. The entries in Table 1 show a range of values of log(K/Q) from −1 to +12; the reaction is thermodynamically unfavorable under some conditions and

TABLE 1: Thermodynamic Feasibility of Reactions with Gaseous Reactants and Products[a]

no.	reaction	Sept noon	Sept midnight	June noon	June midnight	$-\Delta_r H°$	$\Delta_r n$	comment
#1	$2O_3 = 3O_2$ (Figure 1)	48 to 72	48 to 72	48 to 80	46 to 78	+286	+1	favored
#2	$NO + 2HNO_3 = 3NO_2 + H_2O$ (Figure 2)	4 to 11	−1 to 14	0 to 12	0 to 12	−35.1	+1	mixed
#3	$ClO + H_2O = HCl + HOO$	−8 to −4	−9 to −3	−8 to −3	−9 to −3	−50.4	0	forbidden
	Antarctic Reactions							
#4	$ClONO_2 + HCl = Cl_2 + HNO_3$	17 to 20	17 to 21	16 to 22	16 to 22	+67.9	0	favored
#5	$HOCl + HCl = H_2O + Cl_2$	9 to 17	10 to 16	9 to 18	9 to 17	+75.1	0	favored
#6	$N_2O_5 + H_2O = 2HNO_3$	9 to 15	9 to 15	7 to 15	7 to 15	+36.7	0	favored
#7	$ClONO_2 + H_2O = HOCl + HNO_3$ (Figure 3)	2 to 8	2 to 8	1 to 8	1 to 8	−7.2	0	mixed
	Miscellaneous Reactions							
#8	$2HNO_3 + H_2CO = CO_2 + NO + NO_2 + 2H_2O$	72 to 106	78 to 109	72 to 114	76 to 114	+486	+2	favored
#9	$HOBr + HBr = H_2O + Br_2$	15 to 34	15 to 34	15 to 37	15 to 37	+156	0	favored
#10	$N_2O_5 + H_2O_2 = HNO_3 + HOONO_2$	11 to 17	14 to 17	11 to 19	10 to 18	+79.0	0	favored
#11	$HNO_3 + H_2O_2 = H_2O + HOONO_2$	0 to 6	0 to 6	0 to 7	2 to 7	+42.3	0	mixed
#12	$N_2O_5 = NO_3 + NO_2$	−2 to 12	5 to 18	−4 to 14	−4 to 18	−93.5	+1	mixed
#13	$HOONO_2 = HO_2 + NO_2$	−6 to 0	−3 to 4	−6 to 3	−3 to 4	100.7	+1	mixed
#14	$ClONO_2 + H_2O = HCl + HOONO2$	−11 to −3	−11 to −2	−11 to −1	−12 to −3	−108	0	forbidden

[a] The numbers in each cell represent the range of log(K/Q) encountered for that reaction at the specified time and season. $-\Delta_r H°$ in units of kJ/mol.

TABLE 2: Thermodynamic Feasibility for Atmospheric Reactions Producing Photolytically Active Intermediates As Measured by the Range of log[X], When X Is at Chemical Equilibrium with Ambient Reactants and Products[a]

no.	reaction	Sept noon	Sept midnight	June moon	June midnight	comments
	HONO-Producing Reactions					
#15	$H_2CO + 2HNO_3 = CO_2 + 2HONO + H_2O$	47 to 67	47 to 67	47 to 73	47 to 73	always favored
#16	$CO + HNO_3 = CO_2 + HONO$	44 to 64	44 to 64	44 to 68	44 to 68	always favored
#17	$H_2CO + 2NO_2 = 2HONO + CO$	27 to 36	25 to 35	25 to 39	25 to 30	always favored
#18	$HO_2 + NO_2 = HONO + O_2$	22 to 34	22 to 38	20 to 41	24 to 40	always favored
#19	$HOONO_2 = HONO + O_2$	16 to 21	15 to 21	15 to 22	15 to 22	always favored
#20	$NO + HNO_3 = NO_2 + HONO$	7 to 11	0 to 9	2 to 11	0 to 9	favored, Figure 5
#21	$NO + NO_2 + H_2O = 2HONO$	3 to 8	2 to 6	3 to 8	2 to 7	mixed, Figure 5
#22	$2NO_2 + H_2O = HONO + HNO_3$	−2 to 6	−4 to 6	−4 to 6	−4 to 6	not favored, Figure 5
	$ClNO_2$ and Br_2 Reactions					
#23	$N_2O_5 + HCl = HNO_3 + ClNO_2$	10 to 18	5 to 18	7 to 15	9 to 19	always favored
#24	$HNO_3 + HCl = H_2O + ClNO_2$	1 to 7	2 to 7	1 to 7	1 to 7	weakly favored
#25	$HOBr + HBr = H_2O + Br_2$	15 to 34	15 to 34	15 to 37	15 to 37	always favored

[a] All thermochemical data are obtained from ref 2 except K_f(HOBr), which is taken from ref 23. [X] = HONO, $ClNO_2$ or Br_2.

TABLE 3: Thermodynamic Feasibility According to Different Dimensionless Ratios (See Text)[a]

no.	reaction	thermodynamic test	value range	$-\Delta_r H°$	$\Delta_R n$	comment
	Complex Mechanisms					
#26	$HNO_3 + H_2CO = HONO + CO + H_2O$	$\log K_{26}/[H_2O]$	59 to 80	+297.3	+1	strongly favored
#27	$2HONO = NO + NO_2 + H_2O$	$\log K_{26}/[H_2O]$	1.8 to 8.5	−38.5	+1	endothermic
#28	$2HNO_3 + 2H_2CO = NO + NO_2 + 2CO + 3H_2O$ #28 = 2 × #26 + #27	$\log(K_{28}/Q_{28})$	81 to 140	+556.0	+3	strongly favored
#20	$HNO_3 + NO = HONO + NO_2$	K_{20} (not $\log K_{20}$)	8.5 to 14	+1.7	0	weakly favored
#2	#2 = 2 × #20 + #27	$\log(K_2/Q_2)$	0 to 12	−35.1	+1	mixed, Figure 2
	Nitric and Sulfuric Acid Reduction					
#29	$2HNO_3+CH_4 = 2HONO+H_2CO+H_2O$	$\log(K/[H_2O])$	42 to 67	+59.0	+1	strongly favored
#30	$HNO_3 + H_2O_2 = HONO + H_2O + O_2$	$\log(K/[O_2]$	17 to 25	+6.7	+1	strongly favored
#31	$HNO_3 + SO_2 + H_2O = H_2SO_4$ (liq) + HONO	$\log[HONO]/[SO_2]$	1.7 to 32	+220.5	−2	favored, Figure 6
#24	$HNO_3 + HCl = ClNO_2 + H_2O$	K_{24} (not $\log K_{24}$)	8.8 to 21	+3.4	0	weakly favored
#32	H2SO4 (liq) + $H_2CO = SO_2 + CO + 2H_2O$	$\log([SO_2]/[H_2CO]$	25 to 45	−38.2	+3	endothermic
#33	H_2SO_4 (liq) + $2HCl = SO_2 + Cl_2 + 2H_2O$	$\log[SO_2][Cl_2]/[HCl]^2$	−15 to +5	−218.6	+2	not allowed

[a] Nitric acid reduction and sulfuric acid reduction. The range of values is based on profiles at 6, 42, and 71 °N, June noon.

strongly favored under other conditions. In this case, it is interesting to show two-dimensional altitude and latitude plots of log(K/Q) for (a) September noon, (b) September midnight, (c) June noon, and (d) June midnight in Figure 2. Above 30 km altitude in the sunlit atmosphere, including the June summer pole, the reaction is thermodynamically favored to proceed by 8−9 orders of magnitude, but at midnight the modeled Q approaches the equilibrium value. Below 30 km, log(K/Q) is large and positive in the south polar region, day and night at both seasons, and at equatorial and midlatitudes log(K/Q) is +1 at midnight and 5−9 at noon. The low midnight values mean that the concentrations of NO, NO_2, HNO_3, and H_2O are close to their equilibrium values with respect to this reaction. Solar radiation during the daytime increases the [NO]/[NO_2] ratio through ultraviolet photolysis of NO_2 and drives this reaction away from its nighttime near-equilibrium state. Thus, the changes in Figure 2 are not driven by this reaction itself but rather by other chemical and photochemical processes that control the [NO]/[NO_2] ratio. The ambient values of reactants and products are such that this reaction has a strong thermo-

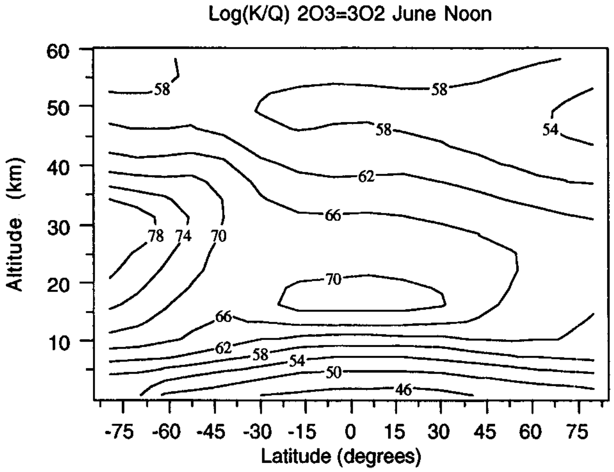

Figure 1. Latitude−altitude plot of $\log_{10}(K/Q)$ for the gas-phase reaction $2O_3 = 3O_2$, modeled at June noon, as a function of altitude and latitude (reaction #1 in Table 1). Over the troposphere and stratosphere, the reaction has an exceedingly strong thermodynamic potential to react at all latitudes, altitudes, times of day, and season. The reaction is strongly exothermic with an average enthalpy of reaction of −286 kJ mol^{-1} between 200 and 300 K.

dynamic potential to occur under sunlit conditions everywhere and at south polar winter and fall conditions, and it has a weak but nonzero thermodynamic potential to occur at night below 30 km altitude.

One use for this method is illustrated with respect to the potential deactivation of atmospheric ClO by heterogeneous catalysis according to reaction #3 of Table 1:

$$\mathrm{ClO + H_2O = HCl + HOO} \qquad (\#3)$$

If this reaction is subjected to the method of this article, it is found to be thermodynamically unfavorable by 3−9 orders of magnitude over the entire troposphere and stratosphere. On this basis, one would reject this reaction with no loss of time and effort in looking for a suitable catalyst.

Catalysts Associated with Antarctic Ozone Loss. For four gas-phase reactions (#4−#7), which are associated with the Antarctic ozone hole, Table 1 summarizes the range of log(*K*/*Q*) in decreasing order of the values of log(*K*/*Q*). For the first three cases, the reactions have a strong thermodynamic tendency to occur at all latitudes, altitudes, and seasons, and yet these reactions do not occur at a measurable rate in the gas phase. As is now well-known,[12−16] these reactions occur at a significant rate by heterogeneous catalysis on atmospheric particles in the south polar winter and spring. The fourth reaction in this group in Table 1, the hydrolysis of chlorine nitrate, has values of log(*K*/*Q*) between 1 and 8, that is, from very weak to strong thermodynamic tendency to occur, and it is interesting to examine the full two-dimensional plots, which are given as Figure 3. The low values occur only in the Austral winter and spring south polar stratosphere, and under some Antarctic conditions, the hydrolysis of chlorine nitrate may be thermodynamically limited. The *K*/*Q* values are at least 1000 over the rest of the troposphere and stratosphere.

Other Atmospheric Processes. Table 1 illustrates the range of log(*K*/*Q*) values for a variety of reactions determined as a function of both daytime and seasonal variations. The additional stratospheric processes in Table 1 are listed in decreasing order of their molar heats of reaction, $-\Delta_r H°$ (eq 17). It is interesting to note the relative role of $-\Delta_r H°$ and $\Delta_r n$ on the magnitude of the thermodynamic tendency to react. The reduction of nitric acid by formaldehyde (reaction #8) is exothermic by 486 kJ mol^{-1}, and there are two more moles of gas in the products than in the reactants. The values of log(*K*/*Q*) vary between 72 and 114, which means that at chemical equilibrium the concentration of at least one of the reactants must approach zero.

Reactions #3−#7, #9−#11, and #14) have $\Delta_r n$ of zero, their average values of log(*K*/*Q*) are plotted against $-\Delta_r H°$ in Figure 4, and there is a strong correlation, which shows that the value of $-\Delta_r H°$ alone could be used as a qualitative guide to their thermodynamic viability. Reactions in Table 1 that have $\Delta n = 1$, have values of log(*K*/*Q*) about 5−10 units higher than those with comparable $-\Delta_r H°$ and with $\Delta n = 0$.

Results with Other Thermodynamic Tests

Thermodynamic Assessment for Species Not Included in LLNL Model. The LLNL model does not include HONO, $ClNO_2$, and Br_2, and Table 2 presents a series of reactions involving these species. In cases such as these where only one species is unobserved, a modified version of the log(*K*/*Q*) method can still provide valuable insight into the thermodynamic viability of a particular process. For example, consider the reaction

$$\mathrm{H_2CO + 2HNO_3 = CO_2 + 2HONO + H_2O} \qquad (\#15)$$

In this case, define Q' as

$$Q = Q'[\mathrm{HONO}]^2 \qquad (22)$$

When the reaction is at thermodynamic equilibrium, $K = Q$, and the concentration of HONO that would, according to this reaction, be in chemical equilibrium with ambient observed or modeled H_2CO, HNO_3, CO_2, and H_2O is

$$[\mathrm{HONOl}_{\mathrm{EQUIL}} = (K/Q')^{1/2} = \left\{\frac{K_{15}([\mathrm{H_2CO}][\mathrm{HNO_3}]^2}{[\mathrm{CO_2}][\mathrm{H_2O}]}\right)^{1/2}_{\mathrm{ACTUAL}} \qquad (23)$$

The values of $[\mathrm{HONO}]_{\mathrm{EQUIL}}$ can be plotted as either a vertical profile or as latitude−altitude contours. We apply this procedure to three species, X = HONO, $ClNO_2$, Br_2, and give results in Table 2.

To decide whether a reaction for these transients is thermodynamically “favored”, we compare the calculated $[\mathrm{Xl}_{\mathrm{EQUIL}}$ against what we regard as an atmospherically important value, which depends on its reactivity and potential for forming active photolytic products, which for [HONO], [$ClNO_2$], or [Br_2] are HO + NO, Cl + NO_2, and Br + Br, respectively. On this basis, we take thermodynamically favored values of [X] to be

$$\log[\mathrm{HONO}] \geq 7$$

$$\log[\mathrm{ClNO_2}] \geq 7$$

$$\log[\mathrm{Br_2}] \geq 5$$

(in molecules cm^{-3}) for the proposed reaction to represent a significant potential source of radical species. Results from this type of analysis, evaluated for log([HONO]), log([$ClNO_2$]), or log([Br_2]) are shown in Table 2.

HONO-Producing Reactions. For five of the reactions (#15−#19) in Table 2, the calculated concentrations of [$\mathrm{HONO}_{\mathrm{EQUIL}}$] are much larger than the atmospheric source material, and thus, we obtain only the qualitative result that these reactions are strongly thermodynamically favored to produce HONO and its photolysis products; the numbers and plots of these cases are not significant. Cases that are weakly favored or are favored in some regions but not in others are plotted as vertical profiles

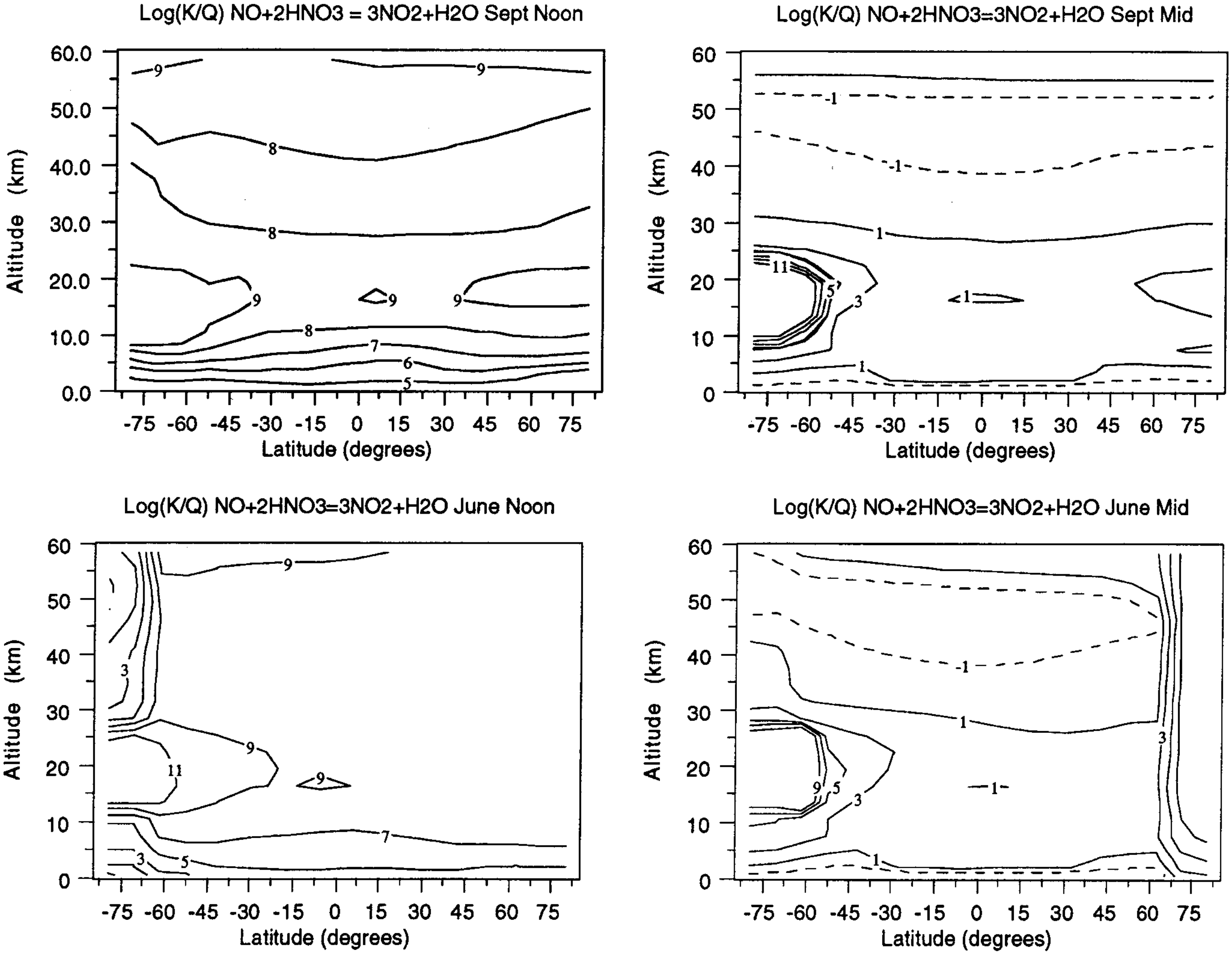

Figure 2. Latitude−altitude plot of $\log_{10}(K/Q)$ for the gas-phase reaction $NO + 2HNO_3 = 3NO_2 + H_2O$ modeled at (a) September noon, (b) September midnight, (c) June noon, and (d) June midnight (reaction #2 in Table 1).

at three representative latitudes for the daytime $\log([HONO]_{EQUIL})$ in Figure 5. Reaction #20, $NO + HNO_3 = HONO + NO_2$, would be a strong source of HONO and thus of OH, if it had a suitable catalyst (Figure 5, right trio of profiles). The formation of HONO by heterogeneous catalysis of reaction #21, $NO + NO_2 + H_2O = 2HONO$, could be important in the boundary layer, but from thermodynamics alone (and in agreement with ref 1 and laboratory results by Saastad et al.[17]), it is seen to be a weak source of OH in the rest of the atmosphere (Figure 5, center trio of profiles). The formation of HONO by heterogeneous catalysis of reaction #22, $2NO_2 + H_2O = HONO + HNO_3$, might be important overnight in heavy urban smog, but from thermodynamics alone, it is seen to be a negligible source of OH in the rest of the atmosphere (Figure 5, left trio of profiles).

Other Thermodynamic Tests. For a reaction with $\Delta_r n$ of zero, the equilibrium constant is dimensionless; it gives the relative probability of products and reactants, and K or $\log K$ is a rough measure of the thermodynamic reaction potential. If $\log K$ is very large, the qualitative evaluation of "strongly favored" is obtained by this simple method. This test would be adequate in making a qualitative judgment of thermodynamic feasibility of reactions #4−#6, #9, #10, #16, #18, #23), all of which have zero $\Delta_r n$ and very large equilibrium constants. An extension of this use of dimensionless ratios is made for some reactions that involve a unit change of $\Delta_r n$. In the troposphere and stratosphere, H_2O is present at concentrations 2 or more orders of magnitude larger than those of NO_y, HO_y, or Cl_y, and $[H_2O]$ will not change significantly upon reaction with these trace species. The essentially constant value of $[H_2O]$ is incorporated in the equilibrium constant. Reaction #26, the first entry in Table 3, is an example:

$$\frac{K_{26}}{[H_2O]_{ACTUAL}} = \left(\frac{[HONO][CO]}{[HNO_3][H_2CO]}\right)_{EQUIL}, \quad \text{dimensionless}$$

This procedure would identify reactions #15, #26, #29 as strongly favored. Since molecular oxygen is in great excess over the trace atmospheric species, an analogous procedure to that used for H_2O can also be employed for reactions involving O_2. Application of this approach with O_2 demonstrates that reaction #30 in Table 3 is strongly favored.

Reaction #31 in Table 3, the formation of HONO from sulfur dioxide and nitric acid, involves two species not included in the LLNL model: HONO and SO_2. Since HONO is a product and SO_2 a reactant, the equilibrium constant expression can be solved for the ratio of the two unknown species, which gives a measure of the local thermodynamic feasibility of the reaction:

$$\frac{[HONO]}{[SO_2]} = K_{31}\frac{[HNO_3]}{[H_2O]} \qquad (24)$$

We evaluate the equilibrium ratio over the two-dimensional space of the model and show vertical profiles of this ratio in Figure 6. This reaction is very strongly favored by thermody-

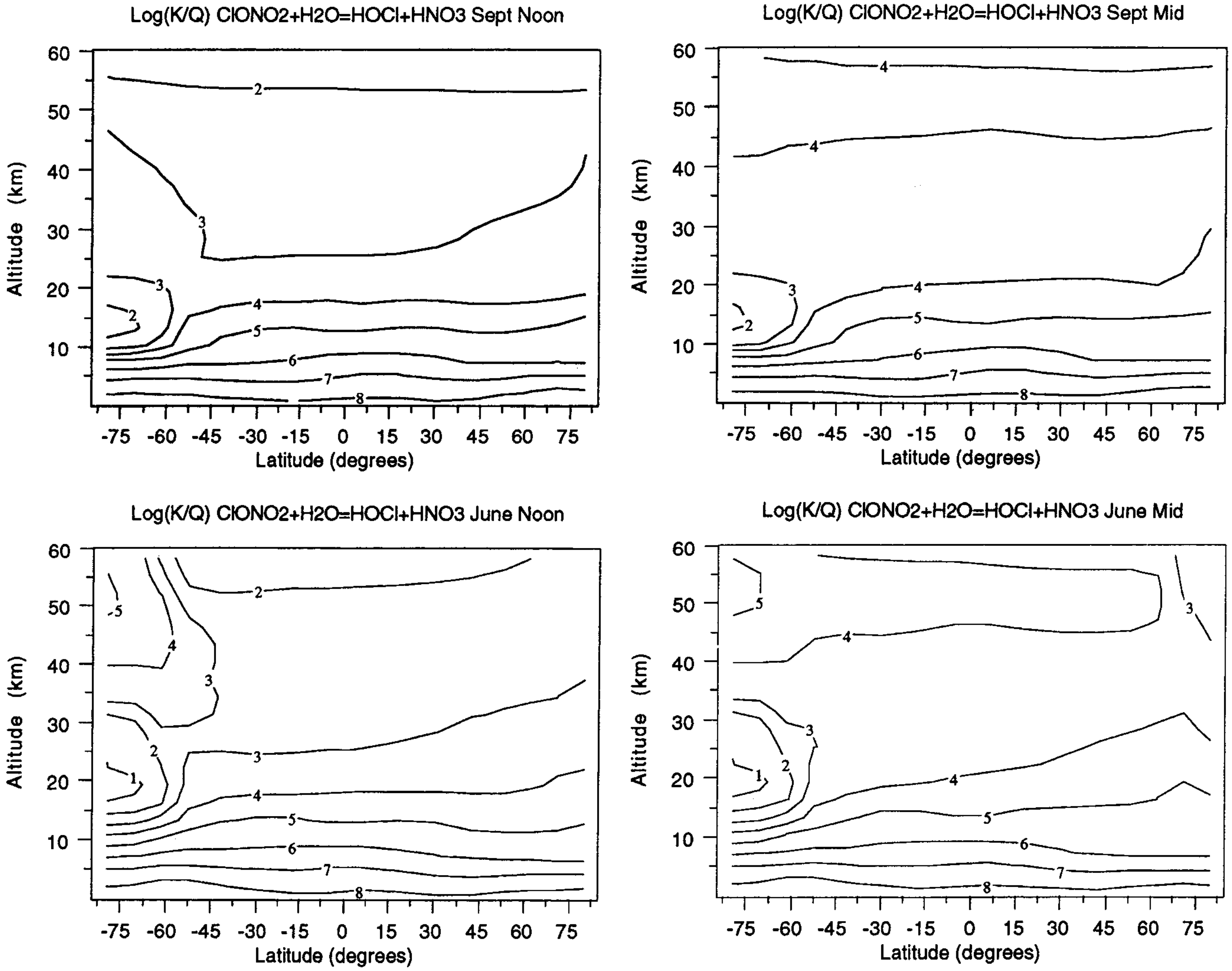

Figure 3. Latitude−altitude plot of $\log_{10}(K/Q)$ for the gas-phase reaction $ClONO_2 + H_2O = HOCl + HNO_3$ modeled at (a) September noon, (b) September midnight, (c) June noon, and (d) June midnight (reaction #7 in Table 1).

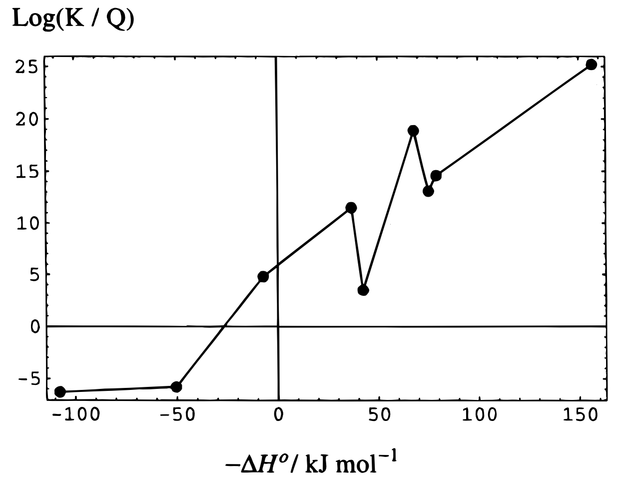

Figure 4. Plot of $\log(K/Q)$ as a function of negative heat of reaction ($-\Delta_r H°$/kJ mol^{-1}) for the nine reactions in Table 1 with no change in number of gas molecules between reactants and products ($\Delta_r n = 0$).

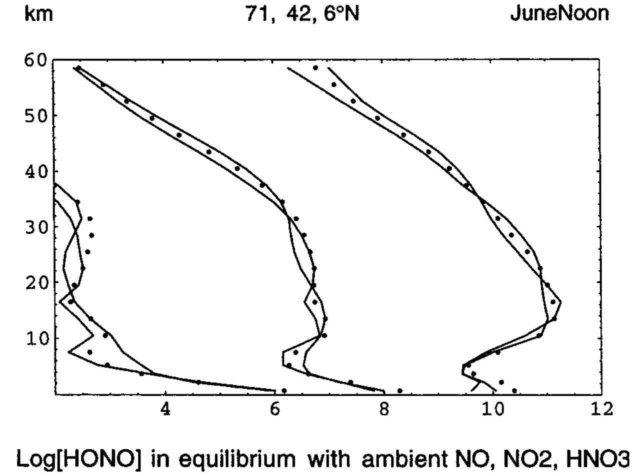

Figure 5. Vertical profiles, triplets at 6, 42, and 71 °N, for each reaction, of the concentration of HONO that would exist if reactions #20, #21, and #22 of Table 2 were in chemical equilibrium with ambient reactants and products of reactions: (left) $2NO_2 + H_2O = HONO = HNO_3$; (middle) $NO + NO_2 + H_2O = 2HONO$; (right) $HNO_3 + NO = HONO + NO_2$.

namics. It is known to occur at room temperature,[18] and it may be important after volcanoes, which eject SO_2 high into the atmosphere.

Discussion

Proposed Mechanisms for Complex Reactions. The reduction of nitric acid by formaldehyde (reaction #8), presumably by heterogeneous catalysis, has one of the strongest thermodynamic potentials of all the reactions studied here: the $\log(K/Q)$ range is 72−114; it is exothermic by 486 kJ mol^{-1}; the number of moles of gas increases by 2. As written, the reaction would require a three-body collision, and it is therefore more reasonable

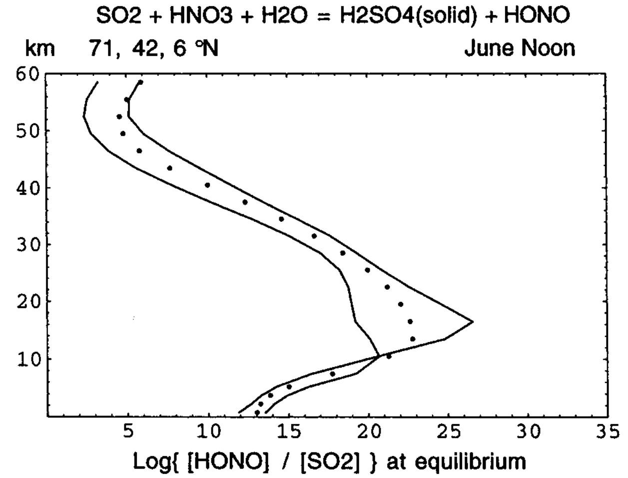

Figure 6. Thermodynamic potential for forming HONO from HNO_3, SO_2, and H_2O (reaction #31 in Table 3). The vertical profiles are the ratio of HONO over SO_2 if there was chemical equilibrium between these two species and ambient HNO_3 and H_2O.

on kinetic grounds to expect that it requires a set of elementary bimolecular steps. Formaldehyde is known to stick to and remain indefinitely in sulfuric acid.[19,20] Jayne et al.[20] suggest a condensed-phase mechanism for the reaction of nitric acid with formaldehyde in sulfuric acid solution, based on room temperature observations, which involves formic acid (HCOOH) as an intermediate. These two steps plus reaction #27 is a mechanism for reaction #8:

$$HNO_3 + H_2CO = HONO + HCOOH \quad \text{all in sulfuric acid solution} \quad (25a)$$

$$HNO_3 + HCOOH = HONO + CO_2 + H_2O \quad (25b)$$

$$2HONO = NO + NO_2 + H_2O \quad (\#27, 25c)$$

$$\text{net:} \quad 2HNO_3 + H_2CO = CO_2 + 2H_2O + NO + NO_2 \quad (\#8)$$

The sum of the first two steps is strongly exothermic, but the third step is endothermic, $\Delta_r H = 38.5$ kJ mol^{-1}, which implies a significant activation energy (eq 18) and a slow rate for the third step at stratospheric temperatures. According to these considerations, the reaction between nitric acid and formaldehyde to form carbon dioxide does not occur as reaction #8 but rather as

$$2HNO_3\,(\text{gas}) + H_2CO\,(\text{solvated}) = 2HONO\,(\text{solvated}) + CO_2\,(\text{gas}) + H_2O\,(\text{gas}) \quad (26)$$

Like reaction 26, reactions #15− #22 are shown as producing HONO in sulfuric acid aerosols, and thus, the interaction between HONO and sulfuric acid needs to be considered.[1] In highly concentrated sulfuric acid, HONO exists in solution as nonvolatile nitronium bisulfate ions, NO^+ and HSO_4^-, and at high concentrations of these ions, they precipitate out as the ionic crystal nitrosyl sulfuric acid. At somewhat lower concentration of sulfuric acid, nitrous acid exists in solution as a hydrated nitronium ion, H_2ONO^+. At still lower concentrations of sulfuric acid it exists as molecular HONO and tends to evaporate out of the sulfuric acid solution. If HONO is formed in the 20−25 km altitude range, where the sulfuric acid percentage is high, the nonvolatile dissolved or precipitated nitronium bisulfate form of nitrous acid could accumulate in sulfuric acid aerosols, and when the particles grow big enough, they begin to settle out into the lower stratosphere and upper troposphere. When the settling aerosol particles take on extra water, positive ionic forms of nitrous acid turn into molecular HONO and evaporate into the atmosphere, where they accumulate overnight and photolyze to OH and NO at sunrise and during the day. This source of HONO would add to the HONO locally formed in the lower stratosphere and upper troposphere, and it might contribute to the extra OH observed.[21,22]

Similarly, reaction #2 can be represented by the sum of bimolecular steps:

$$\text{twice } HNO_3 + NO = HONO + NO_2 \quad (\#20)$$

$$\text{plus } 2HONO = NO + NO_2 + H_2O \quad (\#27)$$

$$\text{net:} \quad 2HNO_3 + NO = 3NO_2 + H_2O \quad (\#2)$$

This reaction has its best chance of occurring in nitric acid-rich sulfate aerosols. Since #27 is 38.5 kJ mol^{-1} endothermic, the reduction of nitric acid by nitric oxide in the stratosphere is expected to be given by reaction #20 rather than by reaction #2. Figure 5 shows that reaction #20 is mildly favored by thermodynamics at altitudes below the middle stratosphere.

Reduction of Nitric Acid and of Sulfuric Acid. There is strong thermodynamic potential for reducing nitric acid through heterogeneous catalysis by methane (reaction #29), formaldehyde (reactions # 8, #15, #26), carbon monoxide (reaction #16), sulfur dioxide (reaction #31, Figure 6), and hydrogen peroxide (reaction #30). Nitric acid is weakly reduced by nitric oxide (reaction #20, Figure 5) but not by hydrogen chloride (reaction #24). Sulfuric acid has a strong thermodynamic tendency to be reduced by formaldehyde (reaction #32) but not by HCl (reaction #33). The possible atmospheric importance of some of these reactions is discussed below.

Methane (reaction #29) and carbon monoxide (reaction #16) have exceedingly strong thermodynamic potentials for reducing nitric acid to HONO. Since methane and carbon monoxide are present in the atmosphere at concentrations many orders of magnitude greater than those of other possible significant reducers of HNO_3 (H_2CO, SO_2, H_2O_2, NO), heterogeneous catalytic reduction of nitric acid by CO or CH_4 might be important, even with a low value of γ, the reaction probability per collision, with nitric acid-rich sulfuric acid aerosols.

Reaction #31, $HNO_3 + SO_2 + H_2O = H_2SO_4(\text{liq}) + HONO$, is known to occur readily at ice temperature,[18] but the products are ionic species $H_2ONO^+HSO_4^-$ (solid or in solution). Upon addition of water, HONO is evolved as a gas. Figure 6 shows the reaction to be strongly thermodynamically allowed from the earth surface to the middle stratosphere. The reaction is exothermic, and thus, it could have no activation energy. The rate of this reaction under atmospheric conditions is not known. If reaction #31 occurs on sulfuric acid aerosols, it might be important after large volcanoes and also at night. The reduction of nitric acid by hydrogen peroxide, $HNO_3 + H_2O_2 = HONO + H_2O + O_2$ (reaction #30), is strongly thermodynamically allowed, and the reaction is exothermic by 6.7 kJ mol^{-1}.

We examine the thermodynamics of the reduction of supercooled liquid sulfuric acid by HCl and by formaldehyde:

$$H_2SO_4\,(\text{liq}) + 2HCl = SO_2 + Cl_2 + 2H_2O \quad (\#33)$$

$$H_2SO_4(\text{liq}) + H_2CO = SO_2 + CO + 2H_2O \quad (\#32)$$

Reduction by HCl is thermodynamically unfavorable in most of the atmosphere, and in addition, the rate must be slow at stratospheric temperatures, since the reaction is endothermic by

219 kJ mol^{-1}. Reduction of sulfuric acid by HCl is thus thermodynamically and kinetically unfavorable. Sulfuric acid has a strong thermodynamic tendency to be reduced by formaldehyde (reaction #32) largely by virtue of the large increase of entropy as one volume of gas goes to four, but the reaction is endothermic by 38 kJ mol^{-1} and probably slow at stratospheric temperatures.

Summary

A purpose of this study is to see if there are additional stratospheric or tropospheric gas-phase chemical reactions that might undergo heterogeneous catalysis. On the basis of their thermodynamic and kinetic characteristics, we regard the following reactions as being reasonable candidates for further laboratory study to see if they undergo heterogeneous catalysis under atmospheric conditions.

on H_2SO_4 aerosols preloaded with H_2CO:

$$HNO_3 + 2H_2CO = 2HONO + CO_2 + H_2O$$

on H_2SO_4 or HNO_3-rich aerosols:

$$HNO_3 + SO_2 + H_2O = H_2SO_4\ (liq) + HONO$$

on HNO_3-rich sulfuric acid aerosols:

$$HNO_3 + CO = HONO + CO_2$$

$$2HNO_3 + CH_4 = 2HONO + H_2CO + H_2O$$

$$HNO_3 + H_2O_2 = HONO + H_2O + O_2$$

$$HNO_3 + NO = HONO + NO_2$$

on cold ice surfaces:

$$N_2O_5 + H_2O_2 = HNO_3 + HOONO_2$$

Formaldehyde H_2CO has an extremely strong thermodynamic tendency to reduce nitric acid to HONO. Formaldehyde is captured and held by sulfuric acid aerosols,[19,20] and consequently, aerosols loaded with H_2CO might react upon collision with nitric acid. Reactions just among NO, NO_2, and H_2O have weak or highly localized thermodynamic potential of forming HONO, and these reactions are not good candidates for heterogeneous catalysis. Where HONO is a product in the cases above, laboratory studies should look for HONO or its reaction products: ionic forms in sulfuric solution and NO and NO_2 in the gas phase.

By use of standard chemical thermodynamics, this article presents a full derivation and extensive use of a relatively new[1] method of interpreting global atmospheric data. As an example of its use, we take a global look at the departure of atmospheric reactions from chemical equilibrium, seeking possible new heterogeneous reactions and demonstrating that some reactions cannot be made to go from reactants to products by catalysis.

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References and Notes

(1) Burley, J. D.; Johnston, H. S. *Geophys. Res. Lett.* **1992**, *19*, 1359, 1363.

(2) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Fruip, D. J.; McDonald, R. A.; Syverud, A. N. JANAF Thermochemical Tables, 3rd ed. *J. Phys. Chem. Ref. Data* **1985**, *14*, 1856.

(3) Molina, M. J.; Molina, L. T.; Kolb, C. E. *Annu. Rev. Phys. Chem.* **1996,** *47*, 327.

(4) Atkins, P. W. *Physical Chemistry*, 4th ed.; W. H. Freeman and Co.: New York, 1990; pp 208−222.

(5) Chapman, S. *Mem. R. Meteorol. Soc.* **1930**, *3*, 103.

(6) Hunt, B. G. *J. Geophys. Res.* **1966**, *71*, 1385.

(7) Crutzen, P. J. *Q. J. R. Meteorol. Soc.* **1970,** *96*, 320. Crutzen, P. J. *J. Geophys. Res.* **1971**, *76*, 7311.

(8) Johnston, H. S. *Science* **1971,** *173*, 522.

(9) Stolarski, R. S.; Cicerone, R. J. *Can. J. Chem.* **1974**, *52*, 1610.

(10) Molina, M. J.; Molina, L. T. *J. Phys. Chem.* **1987**, *91*, 433.

(11) Smith, H. J. *J. Am. Chem. Soc.* **1947**, *69*, 1741.

(12) (a) Solomon, S.; Garcia, R. R.; Rowland, F. S.; Wuebbles, D. J. *Nature* **1986**, *324*, 755. (b) Solomon, S. *Rev. Geophys.* **1988**, *26*, 131.

(13) Crutzen, P. J.; Arnold, F. *Nature* **1986**, *324*, 651.

(14) Molina, M. J.; Tso, T. L.; Molina, L. T.; Wang, F. C. Y. *Science* **1987**, *238*, 1253.

(15) Tolbert, M. A.; Rossi, M. J.; Malhotra, R.; Golden, D. M. *Science* **1987**, 1258.

(16) Hofmann, D. J.; Solomon, S. J. *Geophys. Res. Lett.* **1989**, *94*, 5029.

(17) Saastad, O. W.; Ellermann, T.; Nielsen, C. J. *Geophys. Res. Lett.* **1993**, *20*, 1191.

(18) Coleman, G. H.; Lillis, G. A.; Goheen, G. E. In *Inorganic Syntheses*; Booth, H. S., Ed.; McGraw-Hill: New York,1939; Vol. I, Chapter 5, pp 55−59.

(19) Tolbert, M. A.; Pfaff, J.; Jayaweera, L.; Prather, M. J. *J. Geophys. Res.* **1993**, *98*, 2957.

(20) Jayne, J. T.; Worsnop, D. R.; Kolb, C. E.; Swartz, E.; Davidovits, P. *J. Phys. Chem.* **1996**, *100*, 8015.

(21) Salawitch, R. J.; et al. *Geophys Res. Lett.* **1994**, *21*, 2551.

(22) Zhang R.; Leu, M.-T.; Keyser L. F. *J. Phys. Chem.* **1996**, *100*, 339.

(23) McGrath, M. P.; Rowland, F. S. *J. Phys. Chem.* **1994**, *98*, L4773.