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PRESSURE DISSOCIATION AND HIGH DENSITY ADIABATS

by

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PRESSURE DISSOCIATION AND HIGH DENSITY ADIABATS

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Summary

The effect of pressure dissociation on high density adiabats has been investigated. It is found that it may make a substantial difference at higher densities, as compared to when the pressure effect is neglected in the thermodynamic functions for hydrogen molecule and hydrogen molecular ion.

The persistence of hydrogen molecules at high temperatures and densities (Vardya 1960a) led the author to the concept of pressure dissociation (Vardya 1960b) and finally to include an estimate of pressure dependence in the otherwise only temperature dependent partition functions, equilibrium constants and internal energies for the hydrogen molecule (Vardya 1965b). A similar calculation has now been accomplished for the hydrogen molecular ion (Vardya 1965c). These

functions have been utilized here to investigate the effect of pressure dissociation in high density adiabats.

The adiabats have been computed for a gaseous mixture with the chemical composition corresponding to the solar photosphere (Vardya 1965a). In this mixture, hydrogen has been considered as H_2 , H_2^+ , H^- , H and H^+ , helium as He , He^+ , and He^{++} , and sixteen other elements in neutral and once ionized states.

The pressure and temperature dependent equilibrium constants and internal energies for the hydrogen molecule have been calculated along the lines of Vardya (1965b), except that the v^3 term, where v is the vibrational quantum number, has also been included in the evaluation of the energy of vibration. Similar thermodynamic functions for hydrogen molecular ion have been calculated as in Vardya (1965c). The pressure effect on these functions for the negative hydrogen ion and the hydrogen atom and for heavy elements has not been incorporated. We have also not considered the effect of pressure dependent partition functions on the equation of state, except indirectly as affected by the change in the concentration of the hydrogen molecule and hydrogen molecular ion due to pressure dissociation.

The method of computing the adiabats is along the lines of Vardya (1965a). However, the procedure for the cutoff of H_2 and H_2^+ is somewhat different. The concentration of the hydrogen molecule is set equal to zero when one of the following conditions is satisfied:

(1) the temperature, T , exceeds 10^5 ° K; (2) $n_{H_2} \leq 0.0004$, where n_{H_2} is the fractional abundance of hydrogen nuclei in the form of H_2 ; (3) $\Delta\chi_{H_2} \geq 4.5$ ev, where $\Delta\chi_{H_2}$ is the depression of the continuum of the hydrogen molecule. For the hydrogen molecular ion, the only condition imposed for its cutoff is that $\Delta\chi_{H_2^+} \geq 2.6$ ev, where $\Delta\chi_{H_2^+}$ is the depression of the continuum of the hydrogen molecular ion. Negative hydrogen ion has not been considered for $T > 8000$ ° K. There is no denying that these cutoff conditions are somewhat arbitrary; however, any refinement in them will have to await a better theory.

In computing the adiabats, we have considered the following four cases:

- case (a): H_2 and H_2^+ have been considered without pressure dissociation.
- case (b): H_2 has been considered with pressure dissociation but no H_2^+ considered.
- case (c): H_2 has been considered with pressure dissociation and H_2^+ without pressure dissociation.
- case (d): H_2 and H_2^+ have been considered with pressure dissociation.

In Tables I and II are two adiabats, which have been constructed for the case (d). In these tables, $\log T$, $\log \rho$ and $\log P$ are the logarithmic to the base 10 of the temperature in °K, density in gm/cm³, and the total gas pressure in dyn/cm², respectively, f_{H_2} and f_{H^+} are the fractional number abundances of molecular and ionized hydrogen, respectively, such that $(1-f_{H_2}-f_{H^+})$ gives the combined fractional number

abundances of H , H^- and H_2^+ , $V_{ad} \equiv (d \ln T / d \ln P)_{ad}$ denotes the adiabatic gradient, C_p is the specific heat at constant P per gram of matter, R is the gas constant in ergs/deg mole, and Δx_{H_2} and $\Delta x_{H_2^+}$ give the depression of the continuum of the hydrogen molecule (Vardya 1965b) and the hydrogen molecular ion (Vardya 1965c) in ev, respectively.

In these tables, the abundance of H_2 decreases smoothly to zero with increasing temperature, rather than showing a spurious increase, after reaching a minimum value, at higher temperatures (Vardya 1960a). Similar behavior is exhibited by the hydrogen molecular ion. The maximum fractional number abundance of the hydrogen molecular ion is $\sim 3.7 \times 10^{-4}$ at $\log T=4.3$ in Table I and Table II, it is $\sim 1.5 \times 10^{-4}$ at $\log T=4.15$. The reason, that the maximum build up of the hydrogen molecular ion is less in the higher density adiabat (Table II) than in the lower density adiabat (Table I), is the effect of pressure dissociation. For the same reason, H_2 and H_2^+ disappear at a lower temperature in the higher density adiabat than in the lower density adiabat. As expected (Vardya 1965c), the hydrogen molecular ion is completely pressure dissociated at a lower temperature and pressure than the hydrogen molecule.

Note that when the depression of the continuum is as large as ~ 4.0 ev for H_2 , whose dissociation energy is 4.4763 ev, and ~ 2.4 ev for H_2^+ , whose dissociation energy is 2.468 ev, we have really stretched the approximate method of estimating the pressure dependence to an extreme, where its validity may be highly questionable. Fortunately, this happens when the concentrations of H_2 and H_2^+ are rather small.

Another fact worth noting is that the hydrogen atom starts to ionize before all the hydrogen molecules have been dissociated, even when pressure dissociation has been considered. If this fact is real, it is worth recalling, as noted in Vardya (1960a), that the possibility of the formation of the stable ion H_3^+ exists under these circumstances.

For comparison, we have constructed adiabats for the cases (a), (b) and (c), with the same initial temperature and density as in Table II. The differences between case (d) and case (a), case (d) and case (b), and case (d) and case (c), at a given temperature in the values of $\log \rho$, f_{H_2} , ∇_{ad} and C_p/R are given in Table III. For case (a), the concentration of H_2 was set equal to zero for $\log T > 5.0$, and for cases (b) and (c) for $\log T > 4.6$.

The differences between the various cases are negligible (~ 1 per cent) for $\log T \leq 3.8$, because the pressures are low and the higher vibrational and rotational levels do not contribute significantly at these low temperatures. But as we proceed to higher temperatures, the differences do become fairly large, though some quantities are more affected than the others. Note that these differences are, however, somewhat subject to the arbitrary condition(s) imposed on which the cutoff of H_2 and H_2^+ are based.

Comparing cases (b) and (d), and assuming that the case (d) is the correct one, one finds that the error caused, by the neglect of H_2^+ completely (case (b)), rather than considering it with pressure dissociation (case (d)), is not more than 20 per cent, though in most cases it is far less. In contrast, cases (a) and (c) may differ from

case (d) by more than 100 per cent. Note that cases (a), (b) and (c) give higher densities and lower adiabatic gradients than the case (d).

Concluding, we see that the neglect of pressure dissociation at higher densities and temperatures can have a profound effect on the outcome. The neglect can, not only result in incorrect results, but may also produce some spurious phenomena like the buildup of molecules at high temperatures or can cause discontinuity if the molecules are cut off when they reach their minimum concentration. The question of pressure effect is not confined to molecules alone. It has been known for some time by the name of pressure ionization in the case of atoms. The phenomenon of clustering should not be overlooked either at these densities. In fact, one feels that the phenomena of clustering, pressure dissociation, pressure ionization, and degeneracy should be interconnected by one underlying basic theory. However, because of complications, they have been handled as separate phenomena so far. Perhaps, an approach along the lines of many-body problem may rectify the situation, at least in part.

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Table I

Adiabat for case (d)

log T	log ρ	log P	f_{H_2}	f_{H^+}	∇_{ad}	C_p/R	$\Delta\chi_{\text{H}_2}$	$\Delta\chi_{\text{H}^+}$
3.4	-6.500	4.458	0.840	0.000	0.089	11.311	0.000	0.000
3.5	-5.496	5.062	0.645	0.000	0.089	16.121	0.000	0.000
3.6	-4.601	6.641	0.455	0.000	0.106	16.139	0.000	0.000
3.7	-3.897	7.487	0.299	0.000	0.134	12.892	0.000	0.000
3.8	-3.382	8.138	0.183	0.000	0.179	8.805	0.000	0.002
3.9	-3.019	8.626	0.106	0.000	0.239	5.683	0.002	0.050
4.0	-2.820	8.944	0.054	0.001	0.304	3.912	0.011	0.179
4.1	-2.610	9.263	0.032	0.003	0.326	3.400	0.049	0.450
4.2	-2.395	9.585	0.021	0.012	0.314	3.612	0.160	0.895
4.3	-2.164	9.926	0.014	0.030	0.289	4.133	0.433	1.544
4.4	-1.902	10.300	0.009	0.058	0.277	4.795	1.030	2.444
H_2^+ cut off at log T = 4.45								
4.5	-1.645	10.673	0.004	0.096	0.274	5.175	1.934	--
4.6	-1.399	11.036	0.001	0.140	0.278	5.497	2.972	--
4.7	-1.163	11.389	0.000	0.184	0.288	5.723	3.921	--

Table I (contd.)
H₂ cut off at log T = 4.75

log T	log ρ	log P	f_{H_2}	f_{H^+}	v_{ad}	C_{P}/R	$\Delta\chi_{\text{H}_2}$	$\Delta\chi_{\text{H}^+}$
4.8	-0.939	11.729	0.000	0.224	0.300	5.792	--	--
4.9	-0.728	12.055	0.000	0.260	0.314	5.768	--	--
5.0	-0.529	12.367	0.000	0.291	0.328	5.681	--	--
5.1	-0.342	12.666	0.000	0.318	0.341	5.575	--	--

Table II

Adiabat for Case (d)

log T	log ρ	log P	f_{H_2}	f_{H^+}	V_{ad}	C_p/R	ΔX_{H_2}	ΔX_{H^+}
3.4	-6.000	4.946	0.905	0.000	0.110	7.463	0.000	0.000
3.5	-5.137	5.941	0.741	0.000	0.098	12.089	0.000	0.000
3.6	-4.298	6.919	0.559	0.000	0.109	13.499	0.000	0.000
3.7	-3.605	7.752	0.399	0.000	0.134	11.981	0.000	0.000
3.8	-3.073	8.419	0.273	0.000	0.170	9.183	0.000	0.013
3.9	-2.675	8.946	0.180	0.000	0.220	6.532	0.014	0.208
4.0	-2.470	9.278	0.097	0.000	0.283	4.452	0.079	0.599
4.1	-2.259	9.605	0.055	0.002	0.325	3.443	0.267	1.188
4.2	-2.058	9.918	0.030	0.008	0.335	3.636	0.632	1.887
4.3	-1.851	10.235	0.015	0.021	0.313	3.632	1.232	2.689
H_2^+ cut off at log T = 4.30								
4.4	-1.622	10.575	0.006	0.043	0.297	4.088	2.134	--
4.5	-1.414	10.897	0.002	0.075	0.289	4.575	3.045	--
4.6	-1.184	11.241	0.000	0.111	0.291	4.906	3.983	--

Table II (contd.)

H₂ cut off at log T = 4.65

log T	log ρ	log P	f _{H₂}	f _{H⁺}	v _{ad}	C _P /R	Δx _{H₂}	Δx _{H⁺}
4.7	-0.957	11.582	0.000	0.148	0.298	5.113	--	--
4.8	-0.741	11.912	0.000	0.183	0.308	5.222	--	--
4.9	-0.536	12.231	0.000	0.215	0.320	5.246	--	--
5.0	-0.342	12.537	0.000	0.243	0.333	5.212	--	--
5.1	-0.157	12.832	0.000	0.267	0.344	5.151	--	--

Table III

Comparison of Adiabats for Cases (a), (b), (c) and (d).

log T	log ρ			f_{H_2}			∇_{ad}			C_p/R		
	(d)-(a)	(d)-(b)	(d)-(c)	(d)-(a)	(d)-(b)	(d)-(c)	(d)-(a)	(d)-(b)	(d)-(c)	(d)-(a)	(d)-(b)	(d)-(c)
3.4	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.004	0.	0.
3.5	0.	0.	0.	0.	0.	0.	0.	0.	0.	-0.014	0.	0.
3.6	0.	0.	0.	0.	0.	0.	0.	0.	0.	-0.005	0.	0.
3.7	-0.001	0.	0.	-0.002	0.	0.	0.001	0.	0.	0.019	0.	0.
3.8	0.	0.001	0.001	-0.003	0.	0.	0.	0.	0.	0.032	0.	0.
3.9	0.006	0.005	0.005	-0.006	0.001	0.001	0.001	0.	0.	0.019	0.009	0.008
4.0	0.033	0.037	0.025	-0.008	0.005	0.003	0.004	-0.002	-0.001	-0.093	0.045	0.026
4.1	0.019	-0.009	-0.005	-0.021	0.	0.	0.012	0.002	-0.007	-0.331	0.234	-0.220
4.2	0.009	0.003	-0.021	-0.033	0.	0.	0.022	0.004	0.003	-0.059	0.449	1.015
4.3	-0.009	0.014	0.037	-0.047	0.	0.	0.018	0.005	0.011	-0.386	0.244	-0.053
4.4	-0.030	0.017	-0.068	-0.063	-0.001	0.	0.021	0.002	0.022	-0.396	-0.032	0.044
4.5	-0.095	-0.008	-0.135	-0.084	0.	0.001	0.026	0.	0.032	-0.317	0.018	-0.034
4.6	-0.159	-0.009	-0.202	-0.111	0.	0.	0.036	0.	0.046	-0.229	0.024	0.063
4.7	-0.238	-0.007	-0.291	-0.144	0.	0.	0.047	-0.001	0.059	-0.088	0.020	0.256
4.8	-0.334	-0.007	-0.399	-0.182	0.	0.	0.058	-0.001	0.069	0.084	0.019	0.502
4.9	-0.438	-0.006	-0.514	-0.221	0.	0.	0.069	-0.001	0.077	0.239	0.017	0.718
5.0	-0.549	-0.006	-0.631	-0.261	0.	0.	0.080	0.	0.085	0.360	0.016	0.863
5.1	-0.355	-0.006	-0.748	0.	0.	0.	0.091	0.	0.091	0.825	0.015	0.945