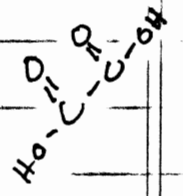
34 pts.

CHM5250 - Assignment #3

(10) (1) Steinfeld 7.14 $F + H_2 \longrightarrow FH + H$



$D_{FH} = 591.1$ kJ/mol $D_{HH} = 458.2$ kJ/mol

$\beta_{FH} = 2.2189$ Å^{-1} $\beta_{HH} = 1.9420$ Å^{-1}

$r^\circ_{FH} = 0.917$ Å $r^\circ_{HH} = 0.7419$ Å

$S_{FH} = 0.167$ $S_{HH} = 0.106$

$$V(r_{FH_1}, r_{H_1H_2}, r_{FH_2}) = \frac{Q_{FH_1}}{1+S_{FH_1}} + \frac{Q_{1-2}}{1+S_{1-2}} + \frac{Q_{F-2}}{1+S_{F-2}} - \left\{ \frac{1}{2}\left[\left(\frac{J_{F-1}}{1+S_{F-1}} - \frac{J_{1-2}}{1+S_{1-2}} \right)^2 + \left(\frac{J_{1-2}}{1+S_{1-2}} - \frac{J_{F-2}}{1+S_{F-2}} \right)^2 + \left(\frac{J_{F-2}}{1+S_{F-2}} - \frac{J_{F-1}}{1+S_{F-1}} \right)^2 \right] \right\}^{1/2}$$

F-H, and F-H_2 will both use the FH set of parameters - it is still an F atom and an H atom.

$r_{F-H_2} = r_{F-H_1} + r_{H_1H_2} = r_{FH} + r_{HH}$

$$Q_{FH_1} + J_{FH_1} = D_{FH_1}\left\{ \exp\left[-2\beta_{FH_1}(r_{FH_1} - r^\circ_{FH_1})\right] - 2\exp\left[-\beta_{FH_1}(r_{FH_1} - r^\circ_{FH_1})\right] \right\}$$

$$Q_{FH_1} - J_{FH_1} = \frac{1}{2} D_{FH_1}\left\{ \exp\left[-2\beta_{FH_1}(r_{FH_1} - r^\circ_{FH_1})\right] + 2\exp\left[-\beta_{FH_1}(r_{FH_1} - r^\circ_{FH_1})\right] \right\}$$

Set this up in Excel!

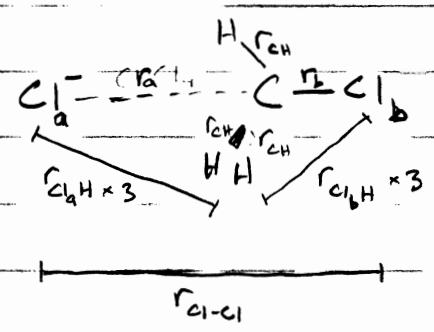
$$Q_{FH_1} = \left[(Q_{FH_1} + J_{FH_1}) + (Q_{FH_1} - J_{FH_1}) \right] \frac{1}{2}$$

$$= \frac{1}{2}\left[D_{FH}\left\{ \exp\left[-2\beta_{FH}(r_{FH} - r^\circ_{FH})\right] - 2\exp\left[-\beta_{FH}(r_{FH} - r^\circ_{FH})\right] \right\} + \frac{1}{2} D_{FH} \times \left\{ \exp\left[-2\beta_{FH}(r_{FH} - r^\circ_{FH})\right] + 2\exp\left[-\beta_{FH}(r_{FH} - r^\circ_{FH})\right] \right\} \right]$$

$$J_{FH} = \frac{1}{2}\left[(Q_{FH} + J_{FH}) - (Q_{FH} - J_{FH}) \right]$$

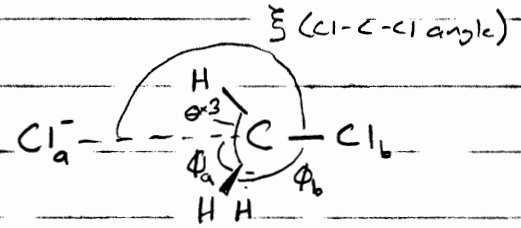
$$= \frac{1}{2}\left[D_{FH}\left\{ \exp\left[-2\beta_{FH}(r_{FH} - r^\circ_{FH})\right] - 2\exp\left[-\beta_{FH}(r_{FH} - r^\circ_{FH})\right] \right\} - \frac{1}{2} D_{FH} \times \left\{ \exp\left[-2\beta_{FH}(r_{FH} - r^\circ_{FH})\right] + 2\exp\left[-\beta_{FH}(r_{FH} - r^\circ_{FH})\right] \right\} \right]$$

(4) (2) a. $Cl^- + CH_3Cl$



$g_a = r_a - r_b$

$g_b = r_b - r_a$



(3) b. $g_a + g_b$ give the difference in C-Cl distances - they measure the extent of reaction. If $g_a = g_b = 0$, then $r_a = r_b$ + rxn. is at the transition state. If $g_a > 0$ (+ $g_b < 0$), $r_a > r_b$ and Cl_a^- has not yet collided w/ the CH_3Cl. If $g_a < 0$ (+ $g_b > 0$), $r_a < r_b$ and Cl_a^- has already collided w/ the CH_3Cl so that the $Cl-Cl_b^-$ distance is now increasing.

(6) c. # coord. = $3N - 6 = 3(6) - 6 =$ **12**

In table 1, eight coords. are defined (less than the minimum), but there are actually three Cl-H distances for each Cl (6 total), three Cl-C-H angles for each Cl (6 total), and three H-C-H angles. This gives a total of:

- $C-Cl_a$
- $C-Cl_b$
- Cl_a-Cl_b
- Cl-H × 6
- C-H × 3
- Cl-C-H × 6
- H-C-H × 3
- Cl-C-Cl

22 coords. → So there are ten redundant coords. plus g_a + g_b (so really 12 red. coord.)

→ It makes sense that many of these are redundant since, for instance, if three Cl-C-H angles and three C-H dist. are defined, then the H-C-H distances are determined by the other parameters → they are geometrically not independent. + can be calc'd by trigonometry

Assignment #3 (cont.)

(2) c. (second c.!) Short + long range discussed in paragraph after eqn (2):

(2) and d. long range: V_{LR}^{a} + V_{LR}^{b} terms (last two terms before D_{mc} + D_c)

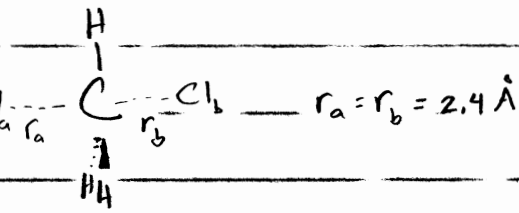
short range: V_{cl} terms (first two terms)
V_ϕ terms (third + fourth terms)
V_{clcl} term (fifth term)
V_θ term (sixth term)
V_{HC} term (seventh term)
} Morse and/or harmonic potential functions

D_{mc}, D_c (bond energies → short range)

(4) e. In the S_N2 reaction described in the paper, there are never any unpaired electrons. The Cl^- ion and CH_3Cl are both closed-shell species. This differs from $H_2 \rightarrow 2H$ in which the reactant is closed shell but the product is open shell. It is the change in pairing of electrons that HF calculations do not deal well with.

(3) f. TS is the maximum on the contour plot in Fig. 7. This is at the point where Cl_a-C = Cl_b-C ($r_a = r_b$). From the plot, this is a distance of ~ 2.4 Å.

Structure:



$r_a = r_b = 2.4$ Å

JFH1 RFH1

RH1H2	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6
0.5	-1296.29	-635.268	-232.07	-78 9799	-26.31	-8.70451	-2.87339	-0.94781	-0.31257	-0.10307	-0.03399	-0.01121
1	-1296 29	-635 268	-232 07	-78 9799	-26 31	-8 70451	-2 87339	-0 94781	-0 31257	-0 10307	-0 03399	-0 01121
1 5	-1296 29	-635 268	-232 07	-78 9799	-26 31	-8 70451	-2 87339	-0 94781	-0 31257	-0 10307	-0 03399	-0 01121
2	-1296 29	-635 268	-232 07	-78.9799	-26 31	-8 70451	-2 87339	-0 94781	-0 31257	-0 10307	-0.03399	-0 01121
2 5	-1296 29	-635 268	-232 07	-78.9799	-26 31	-8.70451	-2.87339	-0 94781	-0 31257	-0 10307	-0 03399	-0 01121
3	-1296 29	-635 268	-232 07	-78 9799	-26 31	-8 70451	-2 87339	-0 94781	-0 31257	-0 10307	-0 03399	-0 01121
3 5	-1296 29	-635 268	-232 07	-78 9799	-26 31	-8.70451	-2 87339	-0 94781	-0 31257	-0 10307	-0 03399	-0.01121
4	-1296 29	-635.268	-232 07	-78 9799	-26 31	-8 70451	-2 87339	-0.94781	-0.31257	-0.10307	-0 03399	-0.01121
4.5	-1296 29	-635 268	-232 07	-78.9799	-26 31	-8 70451	-2 87339	-0 94781	-0 31257	-0 10307	-0 03399	-0 01121
5	-1296 29	-635 268	-232 07	-78 9799	-26 31	-8 70451	-2 87339	-0 94781	-0 31257	-0 10307	-0 03399	-0 01121

JH1H2 RFH1

RH1H2	0 5	1	1 5	2	2 5	3	3 5	4	4 5	5	5 5	6
0 5	-806 312	-806 312	-806 312	-806 312	-806 312	-806 312	-806 312	-806 312	-806 312	-806 312	-806 312	-806 312
1	-374 319	-374 319	-374 319	-374 319	-374 319	-374 319	-374 319	-374 319	-374 319	-374 319	-374 319	-374 319
1 5	-151.647	-151 647	-151 647	-151.647	-151 647	-151 647	-151 647	-151 647	-151 647	-151 647	-151 647	-151.647
2	-58 8478	-58 8478	-58 8478	-58 8478	-58.8478	-58 8478	-58 8478	-58 8478	-58 8478	-58 8478	-58 8478	-58 8478
2 5	-22 4894	-22 4894	-22.4894	-22 4894	-22.4894	-22.4894	-22 4894	-22 4894	-22 4894	-22 4894	-22 4894	-22 4894
3	-8.54599	-8 54599	-8 54599	-8 54599	-8 54599	-8 54599	-8.54599	-8.54599	-8 54599	-8 54599	-8 54599	-8 54599
3 5	-3 24059	-3 24059	-3 24059	-3 24059	-3 24059	-3 24059	-3 24059	-3 24059	-3 24059	-3 24059	-3 24059	-3 24059
4	-1.22782	-1.22782	-1.22782	-1 22782	-1 22782	-1 22782	-1.22782	-1 22782	-1 22782	-1 22782	-1 22782	-1 22782
4 5	-0 46507	-0 46507	-0 46507	-0 46507	-0 46507	-0 46507	-0 46507	-0 46507	-0 46507	-0 46507	-0 46507	-0 46507
5	-0 17614	-0 17614	-0 17614	-0 17614	-0 17614	-0 17614	-0 17614	-0 17614	-0 17614	-0 17614	-0 17614	-0 17614

JFH2 RFH1

RH1H2	0 5	1	1.5	2	2.5	3	3 5	4	4 5	5	5 5	6
0 5	-1074.55	-962.347	-383.434	-133.622	-44.842	-14.8712	-4.91287	-1.62098	-0 53461	-0 17629	-0 05813	-0.01917
1	-962 347	-383.434	-133 622	-44.842	-14.8712	-4.91287	-1 62098	-0 53461	-0.17629	-0.05813	-0 01917	-0 00632
1 5	-383.434	-133 622	-44 842	-14 8712	-4.91287	-1 62098	-0 53461	-0 17629	-0 05813	-0 01917	-0 00632	-0.00208
2	-133 622	-44.842	-14 8712	-4 91287	-1 62098	-0.53461	-0 17629	-0.05813	-0.01917	-0.00632	-0.00208	-0 00069
2.5	-44.842	-14.8712	-4.91287	-1.62098	-0.53461	-0.17629	-0.05813	-0 01917	-0.00632	-0.00208	-0.00069	-0.00023
3	-14.8712	-4 91287	-1.62098	-0.53461	-0.17629	-0.05813	-0.01917	-0.00632	-0.00208	-0.00069	-0 00023	-7.5E-05
3 5	-4.91287	-1.62098	-0.53461	-0.17629	-0.05813	-0 01917	-0.00632	-0 00208	-0.00069	-0 00023	-7 5E-05	-2 5E-05
4	-1.62098	-0.53461	-0.17629	-0 05813	-0.01917	-0.00632	-0.00208	-0.00069	-0.00023	-7 5E-05	-2.5E-05	-8.1E-06
4.5	-0.53461	-0 17629	-0.05813	-0.01917	-0.00632	-0.00208	-0.00069	-0.00023	-7.5E-05	-2.5E-05	-8 1E-06	-2.7E-06
5	-0.17629	-0.05813	-0.01917	-0.00632	-0.00208	-0.00069	-0.00023	-7.5E-05	-2.5E-05	-8.1E-06	-2.7E-06	-8.8E-07

QFH1 RFH1

RH1H2	0.5	1	1.5	2	2.5	3	3 5	4	4.5	5	5 5	6
0.5	2075 506	60 89219	-47 7121	-23 1034	-8 41954	-2.8634	-0.95365	-0.31549	-0.10414	-0.03435	-0.01133	-0.00374
1	2075 506	60.89219	-47 7121	-23.1034	-8 41954	-2 8634	-0.95365	-0.31549	-0 10414	-0.03435	-0 01133	-0 00374
1 5	2075 506	60 89219	-47 7121	-23.1034	-8 41954	-2 8634	-0 95365	-0 31549	-0 10414	-0 03435	-0 01133	-0 00374
2	2075 506	60.89219	-47 7121	-23 1034	-8 41954	-2 8634	-0 95365	-0 31549	-0 10414	-0 03435	-0 01133	-0 00374
2.5	2075 506	60.89219	-47 7121	-23 1034	-8.41954	-2.8634	-0.95365	-0.31549	-0.10414	-0 03435	-0 01133	-0 00374
3	2075 506	60 89219	-47 7121	-23.1034	-8 41954	-2 8634	-0.95365	-0 31549	-0 10414	-0 03435	-0 01133	-0 00374
3 5	2075 506	60 89219	-47 7121	-23 1034	-8 41954	-2 8634	-0 95365	-0 31549	-0 10414	-0 03435	-0 01133	-0 00374
4	2075.506	60.89219	-47 7121	-23 1034	-8 41954	-2.8634	-0 95365	-0 31549	-0 10414	-0 03435	-0 01133	-0 00374
4 5	2075.506	60.89219	-47 7121	-23 1034	-8 41954	-2 8634	-0.95365	-0 31549	-0 10414	-0 03435	-0.01133	-0 00374
5	2075.506	60.89219	-47 7121	-23 1034	-8.41954	-2 8634	-0 95365	-0 31549	-0 10414	-0 03435	-0 01133	-0 00374

QH1H2 RFH1

RH1H2	0 5	1	1 5	2	2.5	3	3 5	4	4 5	5	5 5	6
0 5	512.8584	512.8584	512 8584	512 8584	512 8584	512 8584	512 8584	512 8584	512 8584	512 8584	512 8584	512 8584
1	-12 6742	-12 6742	-12 6742	-12 6742	-12 6742	-12 6742	-12 6742	-12 6742	-12 6742	-12 6742	-12 6742	-12 6742
1 5	-34 4721	-34 4721	-34 4721	-34.4721	-34.4721	-34.4721	-34.4721	-34.4721	-34.4721	-34 4721	-34 4721	-34 4721
2	-17 3103	-17 3103	-17 3103	-17 3103	-17 3103	-17 3103	-17 3103	-17 3103	-17 3103	-17 3103	-17 3103	-17 3103
2 5	-7 16578	-7 16578	-7 16578	-7 16578	-7 16578	-7 16578	-7 16578	-7 16578	-7 16578	-7 16578	-7 16578	-7 16578
3	-2 80124	-2 80124	-2 80124	-2 80124	-2 80124	-2 80124	-2 80124	-2 80124	-2 80124	-2 80124	-2 80124	-2.80124
3 5	-1.07339	-1 07339	-1 07339	-1 07339	-1 07339	-1 07339	-1 07339	-1 07339	-1 07339	-1 07339	-1 07339	-1 07339
4	-0 4083	-0 4083	-0.4083	-0.4083	-0 4083	-0.4083	-0 4083	-0 4083	-0.4083	-0.4083	-0.4083	-0 4083
4 5	-0.15488	-0 15488	-0.15488	-0 15488	-0 15488	-0 15488	-0 15488	-0 15488	-0 15488	-0 15488	-0 15488	-0 15488
5	-0 05869	-0.05869	-0 05869	-0 05869	-0 05869	-0 05869	-0 05869	-0 05869	-0 05869	-0 05869	-0 05869	-0 05869

QFH2 RFH1

RH1H2	0 5	1	1 5	2	2 5	3	3.5	4	4 5	5	5 5	6
0.5	6978 093	476 8809	-41 0826	-35.1107	-13 922	-4 84559	-1 6255	-0 53901	-0 17806	-0.05875	-0.01938	-0.00639
1	476 8809	-41.0826	-35.1107	-13.922	-4.84559	-1.6255	-0.53901	-0.17806	-0.05875	-0.01938	-0 00639	-0 00211
1 5	-41.0826	-35 1107	-13.922	-4.84559	-1 6255	-0 53901	-0 17806	-0 05875	-0 01938	-0 00639	-0 00211	-0 00069
2	-35.1107	-13.922	-4 84559	-1 6255	-0 53901	-0.17806	-0 05875	-0 01938	-0.00639	-0.00211	-0.00069	-0.00023
2.5	-13.922	-4 84559	-1.6255	-0.53901	-0 17806	-0.05875	-0.01938	-0.00639	-0.00211	-0.00069	-0.00023	-7 6E-05
3	-4.84559	-1.6255	-0 53901	-0.17806	-0.05875	-0.01938	-0.00639	-0.00211	-0.00069	-0.00023	-7.6E-05	-2 5E-05
3.5	-1.6255	-0.53901	-0.17806	-0.05875	-0.01938	-0.00639	-0.00211	-0.00069	-0.00023	-7.6E-05	-2 5E-05	-8 2E-06
4	-0 53901	-0.17806	-0 05875	-0 01938	-0 00639	-0.00211	-0.00069	-0.00023	-7.6E-05	-2.5E-05	-8.2E-06	-2.7E-06
4.5	-0 17806	-0.05875	-0.01938	-0.00639	-0.00211	-0.00069	-0.00023	-7 6E-05	-2.5E-05	-8.2E-06	-2.7E-06	-8.9E-07
5	-0.05875	-0.01938	-0.00639	-0 00211	-0.00069	-0.00023	-7.6E-05	-2.5E-05	-8.2E-06	-2 7E-06	-8.9E-07	-2.9E-07

Q+J(FH2) RFH1

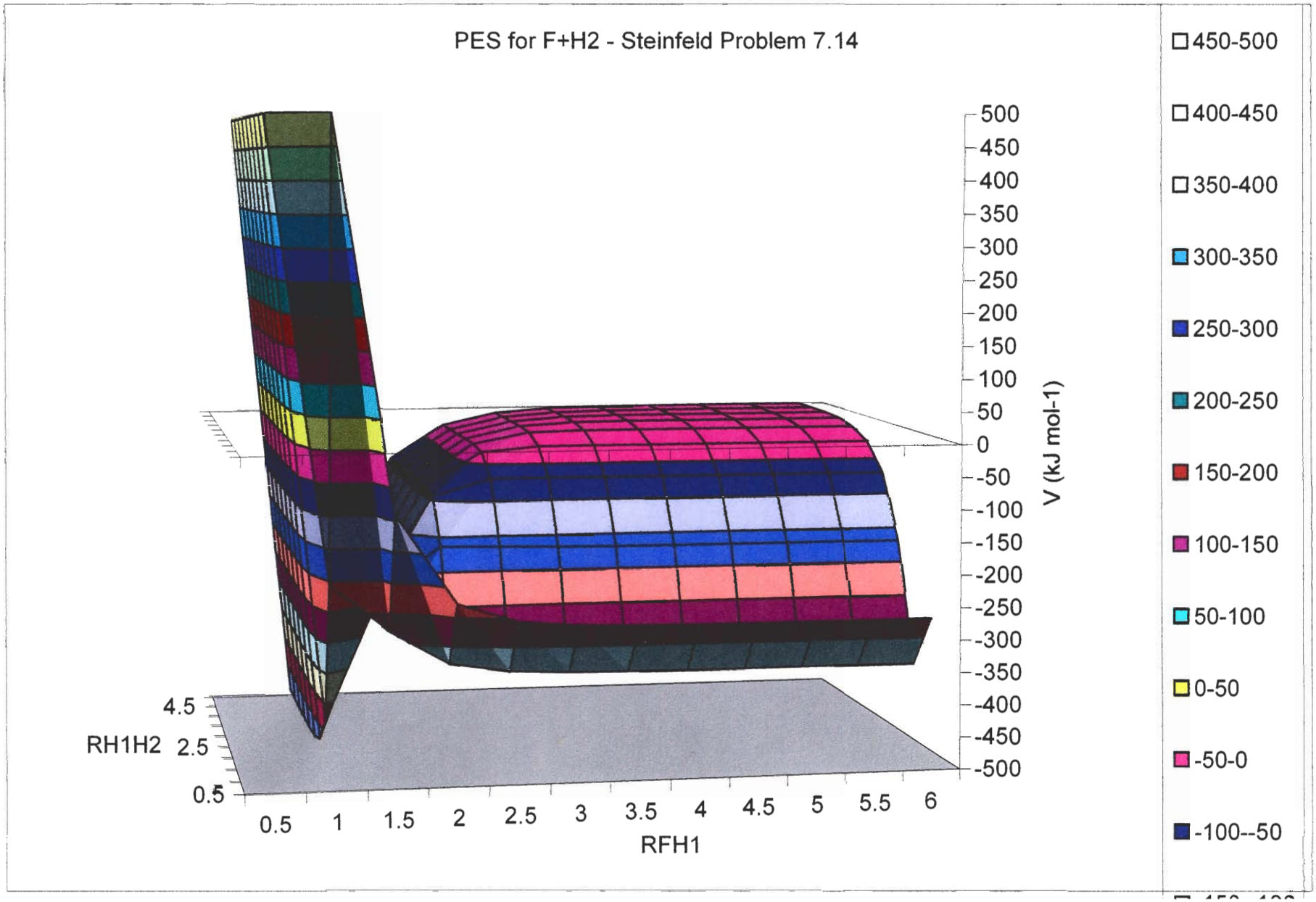
RH1H2	0.5	1	1.5	2	2 5	3	3 5	4	4 5	5	5 5	6
0.5	5903 547	-485.466	-424.517	-168.732	-58.7641	-19.7168	-6.53838	-2.15998	-0.71267	-0.23504	-0.07751	-0.02556
1	-485 466	-424 517	-168 732	-58.7641	-19 7168	-6 53838	-2 15998	-0 71267	-0.23504	-0 07751	-0.02556	-0 00843
1 5	-424 517	-168 732	-58 7641	-19 7168	-6.53838	-2 15998	-0.71267	-0.23504	-0.07751	-0 02556	-0.00843	-0.00278
2	-168 732	-58 7641	-19 7168	-6 53838	-2 15998	-0 71267	-0 23504	-0 07751	-0 02556	-0 00843	-0 00278	-0 00092
2 5	-58 7641	-19 7168	-6 53838	-2 15998	-0 71267	-0 23504	-0 07751	-0 02556	-0 00843	-0 00278	-0 00092	-0 0003
3	-19 7168	-6.53838	-2.15998	-0 71267	-0 23504	-0.07751	-0 02556	-0.00843	-0.00278	-0 00092	-0 0003	-1E-04
3 5	-6 53838	-2 15998	-0 71267	-0 23504	-0 07751	-0 02556	-0 00843	-0 00278	-0 00092	-0 0003	-1E-04	-3.3E-05
4	-2 15998	-0.71267	-0 23504	-0 07751	-0 02556	-0 00843	-0 00278	-0 00092	-0 0003	-1E-04	-3 3E-05	-1 1E-05
4 5	-0 71267	-0 23504	-0 07751	-0 02556	-0.00843	-0 00278	-0.00092	-0 0003	-1E-04	-3 3E-05	-1 1E-05	-3 6E-06
5	-0.23504	-0.07751	-0 02556	-0 00843	-0 00278	-0 00092	-0 0003	-1E-04	-3 3E-05	-1 1E-05	-3.6E-06	-1 2E-06

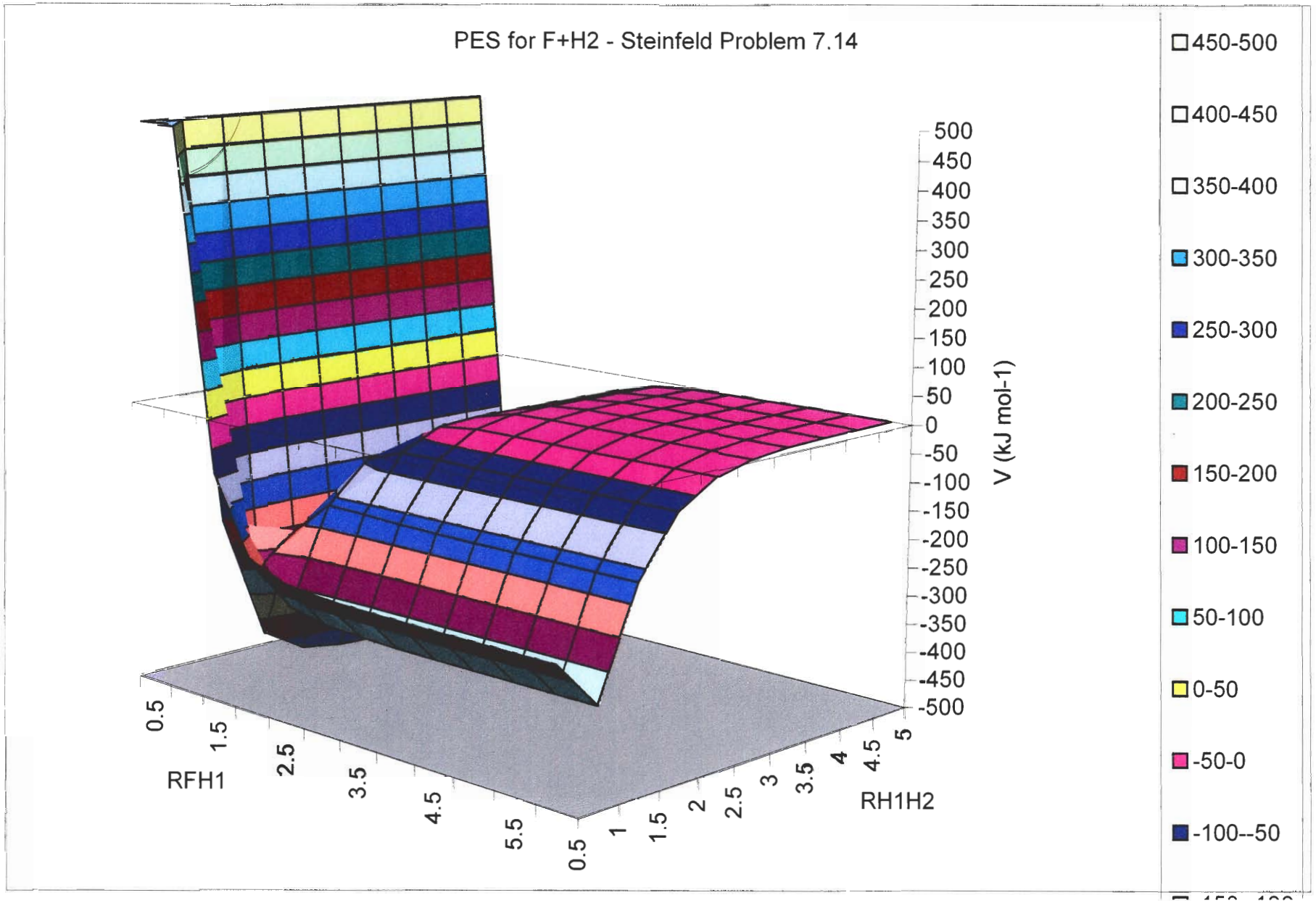
Q-J(FH2) RFH1

RH1H2	0 5	1	1 5	2	2 5	3	3 5	4	4 5	5	5 5	6
0 5	8052 639	1439 228	342 3518	98 5111	30 91999	10 02561	3 287369	1 081969	0 35655	0 117545	0.038757	0 012779
1	1439 228	342.3518	98.5111	30.91999	10 02561	3 287369	1 081969	0 35655	0.117545	0 038757	0 012779	0 004214
1 5	342.3518	98 5111	30.91999	10 02561	3 287369	1 081969	0 35655	0 117545	0.038757	0 012779	0 004214	0 001389
2	98 5111	30.91999	10.02561	3 287369	1 081969	0 35655	0 117545	0 038757	0.012779	0 004214	0 001389	0 000458
2 5	30 91999	10.02561	3 287369	1 081969	0 35655	0 117545	0 038757	0 012779	0 004214	0 001389	0 000458	0 000151
3	10 02561	3 287369	1 081969	0 35655	0 117545	0 038757	0 012779	0 004214	0 001389	0 000458	0 000151	4 98E-05
3 5	3 287369	1 081969	0 35655	0 117545	0.038757	0 012779	0.004214	0 001389	0 000458	0 000151	4 98E-05	1 64E-05
4	1 081969	0 35655	0.117545	0 038757	0 012779	0 004214	0 001389	0 000458	0 000151	4 98E-05	1 64E-05	5.42E-06
4 5	0 35655	0 117545	0 038757	0 012779	0 004214	0 001389	0 000458	0 000151	4 98E-05	1 64E-05	5 42E-06	1 79E-06
5	0 117545	0.038757	0.012779	0.004214	0 001389	0 000458	0 000151	4.98E-05	1 64E-05	5 42E-06	1 79E-06	5 89E-07

V RFH1

R_{H1H2}/R_{FH1}	0.5	1	1 5	2	2 5	3	3 5	4	4.5	5	5 5	6
0 5	7891 105	677 7464	-91 07	-225.411	-254.124	-261 848	-264 204	-264 961	-265.208	-265 289	-265.316	-265.324
1	1499.368	-205 514	-278 327	-329 701	-343 739	-347 928	-349.258	-349 691	-349 834	-349.88	-349 896	-349 901
1.5	818.6544	-428.088	-224 146	-163.069	-164.526	-166.877	-167 802	-168 122	-168.228	-168.264	-168.275	-168.279
2	704.4521	-474.111	-230.234	-94.4537	-68.4552	-67.8785	-68 4585	-68 7191	-68.812	-68.8434	-68.8539	-68.8573
2 5	678.5637	-486.315	-235.867	-85.8759	-34.9148	-26.6821	-26.5048	-26.6864	-26.7686	-26.7981	-26.808	-26 8113
3	671.248	-490.148	-238.259	-86.3787	-29 5267	-12 5497	-10 1801	-10 1563	-10.2182	-10.2453	-10 2549	-10 2581
3.5	668.9124	-491.456	-239.186	-86.9991	-29.4041	-9.92539	-4 51052	-3 86027	-3 86531	-3 88678	-3 89577	-3.89893
4	668.125	-491.92	-239.536	-87.2871	-29.5914	-9.79171	-3.32121	-1.63434	-1.46174	-1.46732	-1.47475	-1.47774
4.5	667 8532	-492.086	-239 667	-87.403	-29.6915	-9.85108	-3.23825	-1 11379	-0.59792	-0.5535	-0.55646	-0.55902
5	667 7582	-492.147	-239.716	-87.4477	-29 7332	-9.88714	-3 25677	-1 06881	-0 37563	-0 22069	-0.20965	-0 21094


PES for F+H2 - Steinfeld Problem 7.14
V (kJ mol-1)
500
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
-500
RH1H2
4.5
2.5
0.5
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
RFH1
450-500
400-450
350-400
300-350
250-300
200-250
150-200
100-150
50-100
0-50
-50-0
-100--50


PES for F+H2 - Steinfeld Problem 7.14
V (kJ mol-1)
500
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
-500
RFH1
0.5
1.5
2.5
3.5
4.5
5.5
RH1H2
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
450-500
400-450
350-400
300-350
250-300
200-250
150-200
100-150
50-100
0-50
-50-0
-100--50