Krypton (Kr)

REFERENCE STATE

\( A_k = 83.80 \)

0 to 6000 K Ideal Monatomic Gas

\[ \Delta H^f(0 \text{ K}) = 0 \text{ kJ mol}^{-1} \]

\[ \Delta H^f(298.15 \text{ K}) = 0 \text{ kJ mol}^{-1} \]

Electronic Levels and Quantum Weights

State \( \epsilon \), cm\(^{-1} \) \( S \)

1s\(_0\) 0 1

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Moore.\(^1\) All predicted levels have been observed for \( n=4 \) but above that many predicted levels are missing. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function\(^2\) has no effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels; the first excited level is nearly 80000 cm\(^{-1}\) above the ground state. Therefore, we list the ground state only.

Extension to higher temperatures may require consideration of excited states and utilization of different fill and cutoff procedures.\(^3\)

The thermodynamic functions at 298.15 K agree exactly with recent CODATA recommendations\(^4\) except for two minor differences

First, the entropy differs by 0.1094 J K\(^{-1}\) mol\(^{-1}\) because this table uses a standard-state pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, entropy differences of the order of 0.001-0.004 J K\(^{-1}\) mol\(^{-1}\) for rare gases arise due to the use of slightly different values for \( R \); this table uses \( R = 8.31441 \text{ J K}^{-1} \text{ mol}^{-1} \). Considering these minor changes, this table agrees within the estimated uncertainty with those by Hultgren et al.\(^4\), Hilborn et al.\(^5\), Garvie et al.\(^6\), and Wagnan et al.\(^7\). The estimated uncertainty is due to uncertainties in the relative atomic masses and fundamental constants which are based on the 1981 scale\(^8\) and the 1973 values,\(^9\) respectively.

Phase Data

The triple point, 115.770 K, and boiling point, 119.800 K, are secondary fixed points of IUPS-68.\(^10\) Hultgren et al.\(^4\) had recommended a triple point of 115.78 K (0.7220 atm) and a boiling point of 119.85 K (1 atm) These values are provided for the convenience of the reader and have not been evaluated by the present authors. As a result of these low values, the reference state for krypton is chosen to be the ideal gas at all temperatures. This may differ from the choice of other authors.

References

$M_e = 63.79945$

**IDEAL GAS**

$$\Delta H^\circ (298.15 K) = 1350.755 \pm 0.012 \text{ kJ mol}^{-1}$$

**Heat of Formation**

The ionization limit of neutral krypton (1291.45 ± 0.01 eV) reported by Moore$^4$ is adopted as $\Delta H^\circ (0 K)$ for Kr(g). The ionization limit is converted from $eV$ to kJ mol$^{-1}$ using the factor, 1 eV = 0.0196262 kJ mol$^{-1}$, which is derived from the latest CODATA fundamental constants.$^5$ The uncertainty in the ionization limit is estimated to be ±0.1 eV which corresponds to an uncertainty of ±0.012 kJ mol$^{-1}$ in the heat of formation. Rosemont et al.$^6$ and Levin and Lias$^7$ have summarized additional ionization potential and appearance potential data.

The recent spectroscopic study by Yoshino et al.$^8$ is in agreement with our adopted value. Durand$^9$ and Wagemann et al.$^{10}$ adopted the same ionization potential, with the exception of the slightly different fundamental constants by Wagemann et al.$^{10}$ which resulted in a heat of formation difference of 0.012 kJ mol$^{-1}$. However, the study by Chaghatai et al.$^{11}$ suggests an ionization potential which is larger by 1 eV.

$\Delta H^\circ (298.15 K)$ is obtained from $\Delta H^\circ (0 K)$ by using IP(Kr) with JANAF$^3$ enthalpies $H^\circ (298.15 K)$ for Kr(g), Kr(1), and Kr(2). (The $\Delta H^\circ (0 K)$ value of Kr(g) is determined by the room temperature threshold energy due to the inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al.$^{12}$ $\Delta H^\circ (298.15 K)$ should be changed by $-6.197 \text{ kJ mol}^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.)

**Heat Capacity and Entropy**

The information on electronic energy levels and quantum weights given by Moore$^4$ is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function$^3$ has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the $\text{P}_2^e$ level, the next lowest level is over 100000 eV above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the ground state and the $\text{P}_2^e$ state, with the energy of the latter state taken from a more recent study by Moore.$^4$ The reported uncertainty in $S^\circ (298.15 K)$ is due to uncertainties in the relative ionic mass and fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and use of different fill and cutoff procedures.$^3$

The thermodynamic functions reported here agree with those of Green et al.$^3$ Hilsenrath et al.$^4$, and Gavan et al.$^2$, except for one or two minor changes. First, the entropy differs by 0.0941 kJ mol$^{-1}$ $\text{K}^{-1}$ because this table uses a standard-state pressure of 1 bar, whereas the cited references specified a pressure of 1 atm. Second, some differences arise from the use of slightly different values for the fundamental constants, the relative ionic mass, and the position of the $\text{P}_2^e$ electronic level.

**References**

3. JANAF Thermochemical Tables: Kr(g), 3-31-92; €(g), 3-31-82.

**Enthalpy Reference Temperature $T_r = 298.15 K$**

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Krypton, Ion (Kr$^+$)

$\text{P}_2^e$ 3531.00 2

$\text{P}_2^e$ 0 4

PREVIOUS March 1977 (1 atm)

CURRENT March 1982 (1 bar)

MALCOLM W. CHASE

Krypton, Ion (Kr$^+$)