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CONSTANTS OR VAPOR PRESSURE WITH TEMPERATURE

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RAPID ESTIMATION OF VARIATION OF EQUILIBRIUM
CONSTANTS OR VAPOR PRESSURE WITH TEMPERATURE.

By

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Abstract

Nomographs have been constructed by which it is possible to estimate rapidly the change in equilibrium constant for any reaction with temperature with a minimum of actual data required. The magnitude of the errors to be expected in the use of the method may also be estimated.

In thermodynamic calculations involving equilibria it is frequently desirable to be able to obtain rapidly approximate values for the constant at various temperatures. For this purpose a nomograph was developed to aid in these calculations. It is most desirable to make use of functions which are as nearly independent of temperature as possible. For any reaction

$$\log K = \frac{-\Delta F^\circ}{2.3 RT} = \frac{1}{2.3 R} \left[\frac{\Delta F^\circ - \Delta H^\circ_{T_0}}{T} \right] - \frac{\Delta H^\circ_{T_0}}{2.3 RT} \quad (1)$$

where K is the equilibrium constant,

ΔF° = the standard free energy change for the reaction

$\Delta H^\circ_{T_0}$ = the standard enthalpy change for the reaction at
reference temperature T_0

R = gas constant per mole

T = absolute temperature

The function

$$\frac{\Delta F^\circ - \Delta H^\circ_{T_0}}{T}$$

changes very slowly with temperature. Thus

$$\frac{\partial \left(\frac{\Delta F^\circ - \Delta H^\circ_{T_0}}{T} \right)}{\partial T} = \frac{-\Delta H^\circ + \Delta H^\circ_{T_0}}{T^2}$$

If the temperature range to be considered is limited such that no phase change occurs in the reactants or products, then

$$\frac{\partial \left(\frac{\Delta F^\circ - \Delta H^\circ_{T_0}}{T} \right)}{\partial T} = \frac{-\Delta c_p (T - T_0)}{T^2}$$

This can be integrated to find the magnitude of the error to be

expected in assuming a constant value of $\frac{\Delta F^\circ - \Delta H^\circ_{T_0}}{T}$. Integrating between T_1 and T_2 using a constant value for Δc_p we obtain

$$\frac{\Delta F^\circ_{T_2} - \Delta H^\circ_{T_0}}{T_2} - \frac{\Delta F^\circ_{T_1} - \Delta H^\circ_{T_0}}{T_1} = -\Delta c_p \left[\frac{T_0}{T_2} - \frac{T_0}{T_1} + \ln \frac{T_2}{T_1} \right]$$

Figure 1 illustrates the error that may be incurred by using a constant value for the function $\frac{\Delta F^\circ - \Delta H^\circ_{T_0}}{T}$. It can be seen that as long as the absolute values of T_1 or T_2 are not over a factor of 3 less or a factor of 6 more than the reference temperature then the maximum error that can be introduced in $\frac{\Delta F^\circ - \Delta H^\circ_{T_0}}{T}$ is in the order of magnitude of $-\Delta c_p$. An error of one cal./degree in $\frac{\Delta F^\circ - \Delta H^\circ_{T_0}}{T}$ produces an error in $\log K$ of 0.219, which although severe for exact calculations is satisfactory for approximate calculations where only the order of magnitude is desired.

Let us calculate the error introduced in calculation of $\frac{\Delta F^\circ - \Delta H^\circ_{T_0}}{T}$ at T_4 by a phase change alone where one of the products of the reaction absorbs an amount of heat ΔH_3 at a temperature T_3 . Integrating as before we obtain

$$\frac{\Delta F^\circ_{T_4} - \Delta H^\circ_{T_0}}{T_4} - \frac{\Delta F^\circ_{T_3} - \Delta H^\circ_{T_0}}{T_3} = \frac{-\Delta H_3(T_4 - T_3)}{T_3 T_4} = -\Delta S_3 \left(1 - \frac{T_3}{T_4}\right)$$

and thus it is apparent that the maximum error that can be introduced from this alone is minus the entropy of the phase change itself as long as T_4 is greater than T_3 . Although this is not too large for a fusion process (~ 1 to 3 e.u./gm. atom) it is rather large for a

vaporization process ($\sim 20 - 25$ e.u. mole). It is thus apparent that whereas one might tolerate the neglecting of Δc_p one should usually correct for a fusion process and always for a vaporization process. This is of course quite easy to do and will be described later. It thus appears that although the chosen function is not perfect it will be satisfactory for rapid calculation and indeed may be corrected for more precise calculations.

Accordingly Figures 2 and 3 were constructed by the methods of Allcock and Jones¹ for solution of equation 1. For any chosen reference temperature T_0 , if any two of $\frac{\Delta F^\circ - \Delta H^\circ_{T_0}}{T}$, $\Delta H^\circ_{T_0}$ or a value of the equilibrium constant are available it is then possible to read values of K versus temperature by using the values of $\frac{\Delta F^\circ - \Delta H^\circ_{T_0}}{T}$ and $\Delta H^\circ_{T_0}$ as pivot point. It should be noted that at T_0

$$\frac{\Delta F^\circ - \Delta H^\circ_{T_0}}{T} = - \Delta S^\circ_{T_0}$$

When it is necessary to evaluate an equilibrium constant beyond where a phase change takes place it is easy to correct for the error which might otherwise be introduced by changing the reference temperature T_0 to the value at the temperature where phase change occurs. It is usually sufficiently accurate to estimate the magnitude of the change in ΔS and noting that K is a continuous function and remembering that

$$\Delta S_{T_0} = - \frac{\Delta F^\circ - \Delta H^\circ_{T_0}}{T_0}$$

move the pivot point along a line joining K and the new T_0 to the new value of $\frac{\Delta F^\circ - \Delta H^\circ_{T_0}}{T}$.

In the use of any such calculation it is very necessary not to overlook the possible presence of species other than the ones under immediate consideration. Although not in significant amounts at one temperature such a species may easily be the predominant one at some other temperature.

Vapor Pressure

Since vapor pressure is merely a special case of equilibrium, Figure 1 has been modified to indicate the values of the entropy of vaporization at the boiling point as given by Trouton's rule $\Delta S_{T_b} = -21$ and by the Kistyakowski Equation³ $\Delta S_{T_b} = 8.75 + 4.57 \log T_b$. Practical use of the nomographs is restricted to low values of the pressure such that the Clausius - Clapeyron equation is applicable.

Example

Calculate the main gaseous liquid and solid phases that will be present versus temperature, if one starts with CoCl_2 and heats it from room temperature to 3000°K . The following data are available.²

	ΔH°_{298} kilocalories	$\frac{\Delta F^\circ - \Delta H^\circ_{298}}{T}$ cal./ $^\circ\text{K}$. per mole at 298
$\text{Cl(s)} + \text{Cl}_2 \longrightarrow \text{CoCl}_2 \text{ (s)}$	- 74	34.7
$\text{Cl} \longrightarrow \frac{1}{2} \text{Cl}_2$	- 28.85	+ 12.8

	Temp. °K.	ΔS Calories/°K. per mole
$\text{CoCl}_2 \text{ (s)} \longrightarrow \text{CoCl}_2 \text{ (l)}$	1000	7.4
$\text{CoCl}_2 \text{ (l)} \longrightarrow \text{CoCl}_2 \text{ (g) 1 atm}$	1323	20.5
$\text{Co (s)} \longrightarrow \text{Co (l)}$	1768	2.1
$\text{Co (l)} \longrightarrow \text{Co (g) 1 atm}$	3370	28

With the above data and the use of Figures 2 or 3 it is possible to read the following equilibrium constants.

	Equilibrium Constant						
Reaction Temp. °K.	298	500	1000	1500	2000	2500	3000
$\text{Co} + \text{Cl}_2 \longrightarrow \text{CoCl}_2$	$> 10^{30}$	$10^{25.8}$	$10^{8.6}$	$10^{4.1}$	$10^{2.4}$	$10^{1.3}$	$10^{0.6}$
$\text{Cl} \longrightarrow \frac{1}{2} \text{Cl}_2$	$10^{18.3}$	$10^{9.8}$	3.2×10^3	25	2.2	0.5	0.2
Vapor Pressure Cobalt atm.					10^{-4}	10^{-2}	0.2
Vapor Pressure CoCl_2 atm	$< 10^{-5}$	atm	4×10^{-2}				

As a check on the error inherent in the calculation an exact calculation of the equilibrium constant for the reaction $\text{Cl} \longrightarrow \frac{1}{2} \text{Cl}_2$ at 2000°K.² is 1.33, an error in log K of -.22 or $\frac{\Delta F^\circ - \Delta H^\circ_{298}}{T}$ of 1.0. One would predict that Δc_p should be from -0.5 to -1.5 cal/°K. mole, depending on whether the vibrational contribution to the heat capacity was complete or near zero. Since $T_2/T_1 = 2000/298 = 6.7$ and $T_1/T_0 = 1$, the predicted error in $\frac{\Delta F^\circ - \Delta H^\circ_{298}}{T}$ in going to 2000° would be from + 0.54 to 1.57 or about $1 \pm .5$, in good agreement with the observed error. With these constants and a few simple calculations the following species are seen to exist, to the nearest order of magnitude.

At 3000°K. Co(l) is certainly the liquid species and no solid can exist. The pressure of cobalt gas is about 0.2 atmospheres and

$$\frac{\text{CoCl}_2}{\text{Cl}_2} = 10^{0.6} = 4 \text{ and } \frac{\text{CoCl}_2}{(\text{Cl})^2} = 4 \times (0.2)^2 = .16. \text{ Therefore, if}$$

Cl = .8 atm, $\text{CoCl}_2 = .10$ atm. Hence Cl is $\sim .7$ atm and $\text{CoCl}_2 \sim .08$ atm, and $\text{Cl}_2 \sim \frac{.08}{4} \sim .02$ atm.

Summarizing in very round numbers:

T = 3000°K.

$$\text{Cl} = 0.7 \text{ atm}$$

$$\text{Co} = 0.2$$

$$\text{CoCl}_2 = 10^{-1}$$

$$\text{Cl}_2 = 10^{-2}$$

Similarly at 2500°K.

Co is liquid species

Gases:

$$\text{CoCl}_2 = .6 \text{ atm}$$

$$\text{Cl} = .4$$

$$\text{Cl}_2 = 10^{-2}$$

$$\text{Co} = 10^{-2}$$

At 2000°K.

Co is liquid species

Gases:

$$\text{CoCl}_2 = 1 \text{ atm}$$

$$\text{Cl} = 10^{-1} - 10^{-2}$$

$$\text{Cl}_2 = 10^{-2} - 10^{-3}$$

$$\text{Co} = 10^{-4}$$

At 1500°K.

Co is solid

Gases:

$\text{CoCl}_2 = 1 \text{ atm}$

$\text{Cl} = 10^{-3} - 10^{-4}$

$\text{Cl}_2 = 10^{-4}$

Below 1323°K. the major gaseous species is CoCl_2 in contact with CoCl_2 solid or liquid. Thus at 1000° the pressure of CoCl_2 is 4×10^{-2} atm over the solid or liquid. Also at 1000° the pressure due to Cl_2 or Cl is below 10^{-6} atm. At 500°K. CoCl_2 exists as a solid with less than 10^{-5} atm pressure of anything.

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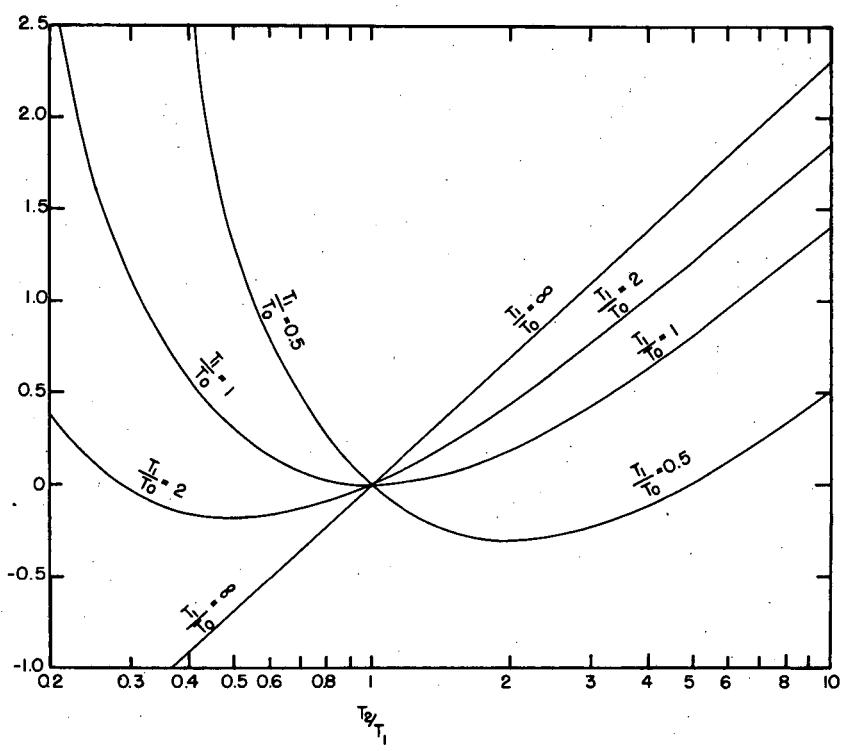


FIGURE 1. FACTOR BY WHICH TO MULTIPLY $-\frac{\Delta C_p}{T}$ TO OBTAIN THE CHANGE IN $\Delta F^\circ - \Delta H^\circ_{T_0}$ IN GOING FROM TEMPERATURE T_1 TO TEMPERATURE T_2 . (NO PHASE CHANGES BETWEEN T_0 AND T_1 OR T_2)

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FIG 1

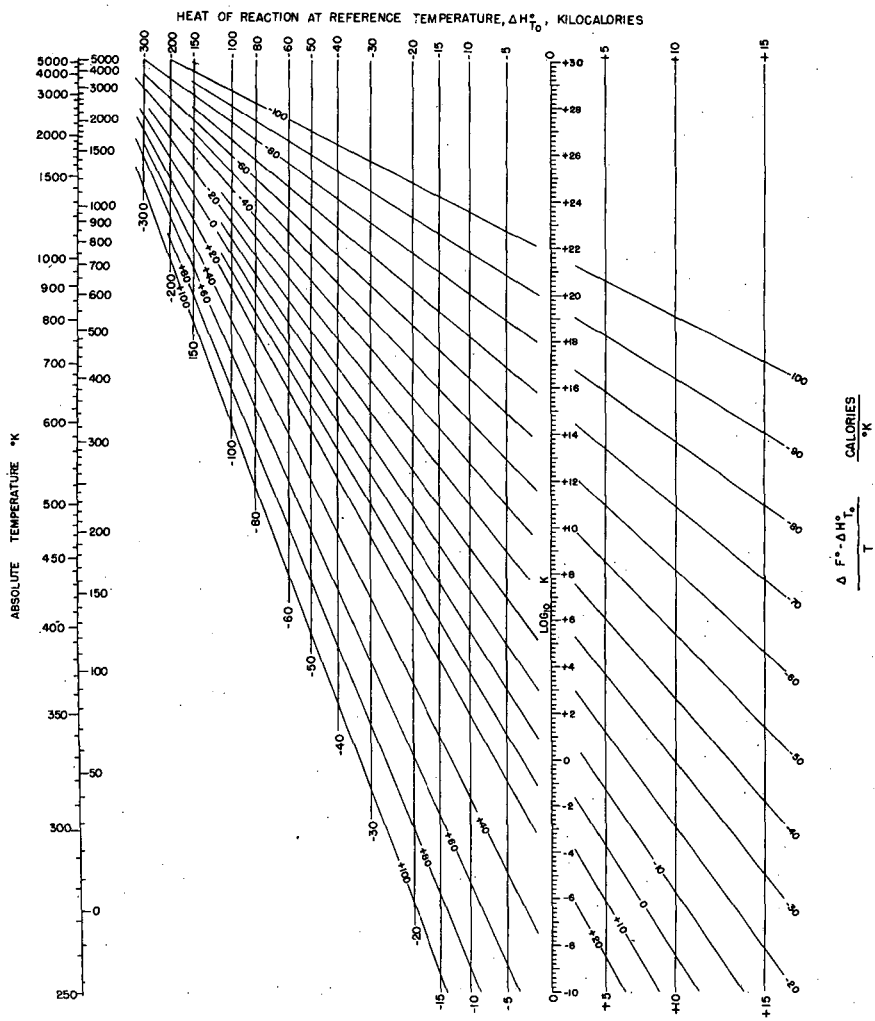


FIGURE 2 VARIATION OF EQUILIBRIUM CONSTANT WITH TEMPERATURE, LARGE VALUES
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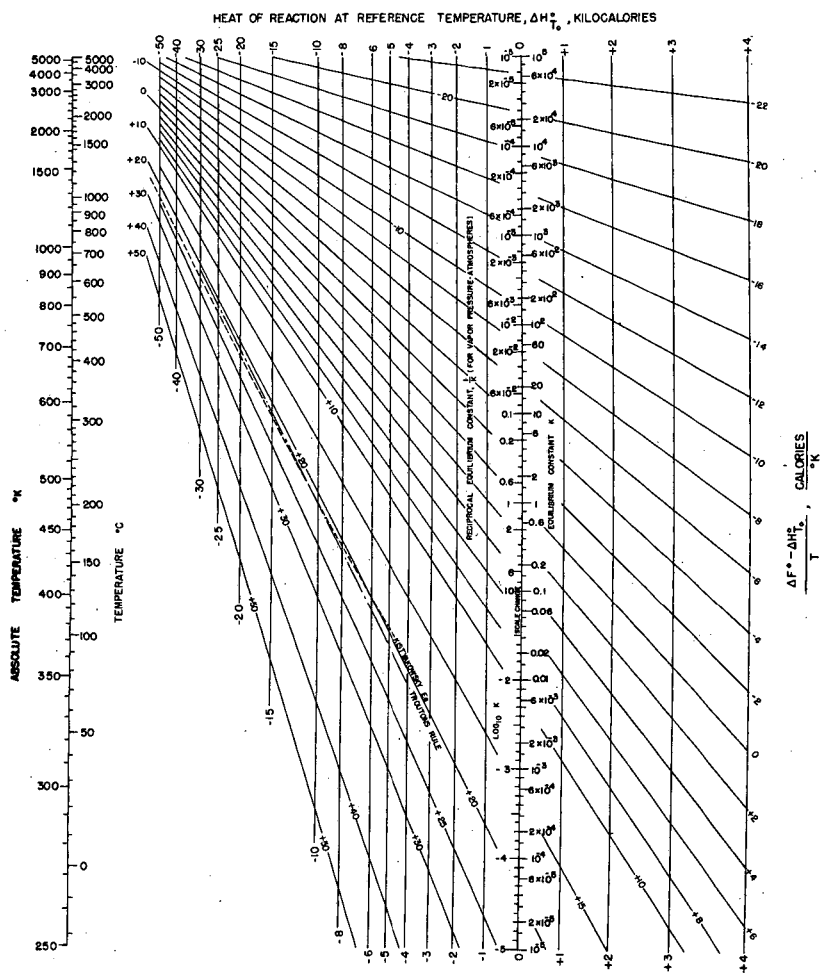


FIGURE 3 VARIATION OF EQUILIBRIUM CONSTANT OR VAPOR PRESSURE WITH TEMPERATURE, VALUES NEAR UNITY

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