EXAMPLE

For the reaction:

$C(graphite) + 2H_2(g) \rightarrow CH_4(g)$

the change in enthalpy is -21 045 cal mol^{-1} at 600°C.

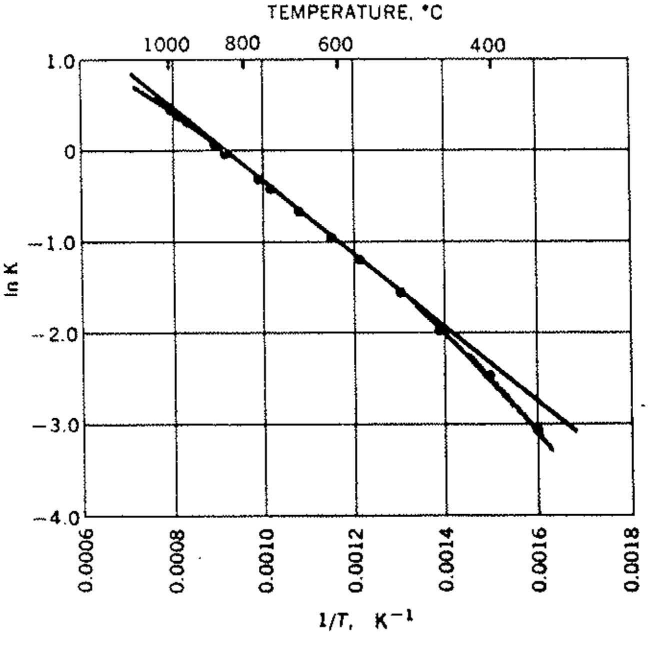
The third law entropies (cal mol^{-1} K^{-1} at 600°C and 1 atm are:

4.98 for C(graphite)
38.9 for $H_2(g)$
56.6 for $CH_4(g)$

(a) Calculate the equilibrium constant for the reaction at 600°C.

(b) What experimental information would you need, besides that given above, in order to be able to evaluate K_p at any temperature? Make a suitable approximation that is adequate over a short temperature range and use it to estimate the equilibrium constant at 750°C.

(b) For the all-gas reaction $CO_2 + H_2 = CO + H_2O$ the temperature dependence has been measured.



The temperature dependence of the equilibrium constant for the reaction $CO_2 + H_2 \rightleftarrows CO + H_2O$

Determine $\Delta_{rxn}H^{\ominus}$ for this reaction at 600 °C.
Describe the states that this $\Delta_{rxn}H^{\ominus}$ corresponds to.

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(a) Calculate the equilibrium constant for the reaction at 600°C.

$$\Delta_{rxn}\boldsymbol{G}^{\ominus}_{T} = -RT \ln K_p$$

$$\Delta_{rxn}\boldsymbol{G}^{\ominus}_{T} = \Delta_{rxn}\boldsymbol{H}^{\ominus}_{T} - T\Delta_{rxn}\boldsymbol{S}^{\ominus}_{T}$$

$$\Delta_{rxn}\boldsymbol{S}^{\ominus}_{T} = \boldsymbol{S}^{\ominus}_{\mathrm{CH4},\,T} - 2\boldsymbol{S}^{\ominus}_{\mathrm{H2},T} - \boldsymbol{S}^{\ominus}_{\mathrm{graphite},\,T}$$

$$\Delta_{rxn}\boldsymbol{S}^{\ominus}_{873} = 56.6 - 2(38.9) - 4.98 = -26.18 \text{ cal mol}^{-1}\text{ K}^{-1}$$

$$\Delta_{rxn}\boldsymbol{H}^{\ominus}_{873} = -21045 \text{ cal mol}^{-1}$$

$$\Delta_{rxn}\boldsymbol{G}^{\ominus}_{873} = -21045 - (873)(-26.18) = 1810 \text{ cal mol}^{-1}$$

$$= -RT \ln K_p$$

$$-\ln K_p = 1810/(1.987)(873) = 1.0435$$

$$K_p = 0.352$$

(b) Estimate the equilibrium constant at 750°C.

Consider $\boldsymbol{G/T}$:

$(\partial(\boldsymbol{G}/T)/\partial T)_p = -(\boldsymbol{G}/T^2) + (1/T)(\partial \boldsymbol{G}/\partial T)_p$

using $\boldsymbol{G} \equiv \boldsymbol{H} - T\boldsymbol{S}$

$(\partial(\boldsymbol{G}/T)/\partial T)_p = -(\boldsymbol{H}/T^2) \quad +(S/T) + (1/T)(\partial \boldsymbol{G}/\partial T)_p$

Recall that: $(\partial \boldsymbol{G}/\partial T)_p = -\boldsymbol{S}$

Thus, $(\partial(\boldsymbol{G}/T)/\partial T)_p = -(\boldsymbol{H}/T^2)$

Combine equations like this for each of reactants and products:

$(\partial(\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}{}_T/T)/\partial T)_p = -(\Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus}{}_T/T^2)$

$\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}{}_T = -RT\ln K_p$

$\therefore (\partial \ln K_p/\partial T)_p = (\Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus}{}_T/RT^2)$

Integrating we get

$\int \mathrm{d}\ln K_p = \int (\Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus}{}_T/R\,T^2)\mathrm{d}T$

We need to know the T dependence of $\Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus}{}_T$.

(for that we need heat capacities of reactants and products).

If we assume that the change with T is small, then approximately,

$$\int \mathrm{d}\ln K_p = +(\Delta_{\text{rxn}}\boldsymbol{H}^{\ominus}_T / R) \int T^{-2}\,\mathrm{d}T$$

the integral $\int T^{-2}\,\mathrm{d}T$ is $-\{(1/T_2) - (1/T_1\}$

$$\ln (K_{p,\,1023} / K_{p,\,873})$$

$$= (\Delta_{\text{rxn}}\boldsymbol{H}^{\ominus}_T / R)\{ (1/873) - (1/1023)\}$$

$$= (-21045 \text{ cal mol}^{-1}/1.987)$$

$$\times\{ (1/873) - (1/1023)\}$$

$$= -1.779$$

$$\therefore \quad (K_{p,\,1023} / K_{p,\,873}) = 0.169$$

$$K_{p,\,1023} = 0.0594$$

On the other hand, suppose we had been given the following data. The heat capacities (cal mol^{-1} K^{-1} in the range 600-750°C and 1 atm) are:

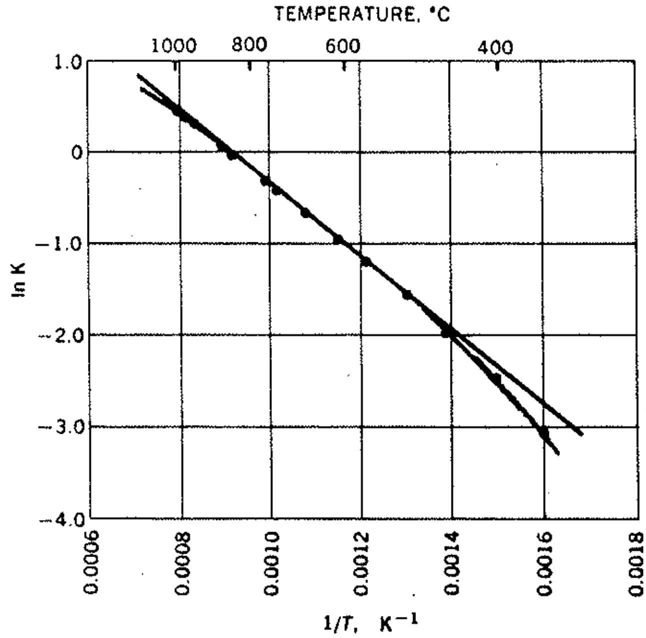
2.038 for C(graphite)
6.888 for H_2(g)
8.438 for CH_4(g)

$\mathrm{C(graphite,\ 873\ K)} + 2\mathrm{H_2(g,\ 873\ K)} \rightarrow \mathrm{CH_4(g,\ 873\ K)}$
$-\ \{\mathrm{C(graphite,\ 873\ K)} \rightarrow \mathrm{C(graphite,}\ T)\}$
$-2\{\mathrm{H_2(g,\ 873\ K)} \rightarrow \mathrm{H_2(g,}\ T)\}$
$\underline{+\ \{\mathrm{CH_4(g,\ 873\ K)} \rightarrow \mathrm{CH_4(g,}\ T)\}\qquad\qquad\qquad}$
$\mathrm{C(graphite,}\ T\ \mathrm{K)} + 2\mathrm{H_2(g,}\ T) \rightarrow \mathrm{CH_4(g,}\ T)$

$$\Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus}{}_{T} = \Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus}{}_{873\,K} - \int_{873}^{T} C_p^{\,C}\mathrm{d}T$$
$$-2\int_{873}^{T} C_p^{\,H2}\mathrm{d}T + \int_{873}^{T} C_p^{\,CH4}\mathrm{d}T$$

$$\Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus}{}_{T}\ \mathrm{cal\ mol}^{-1} = -21045 - 2.038(T-873)$$
$$- 2\times 6.888(T-873) + 8.438(T-873)$$
$$= -21045 + 7.376(873) - 7.376T$$
$$= -14605.7 - 7.376T$$
$$\int \mathrm{d}\ \ln K_p = \int_{873}^{1023} (\Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus}{}_{T} / R\ T^2)\mathrm{d}T$$
$$= \int [-14605.7 - 7.376T]/1.987\ T^2\,\mathrm{d}T$$
$$= \int (-14605.7/1.987)\mathrm{d}(-1/T)$$
$$+ \int (-\ 7.376/1.987)\mathrm{d}(\ln T)$$
$$= +7350.6[(1/1023)-(1/873)]$$
$$-\ 3.708\ \ln[1023/873]$$
$$\int \mathrm{d}\ \ln K_p = -1.2346 - 0.5879 = -1.8225$$
$$\ln\,(K_{p,\ 1023}/K_{p,\ 873}) = -1.8225$$
$$(K_{p,\ 1023}/K_{p,\ 873}) = 0.162 \qquad K_{p,\ 1023} = 0.0569$$

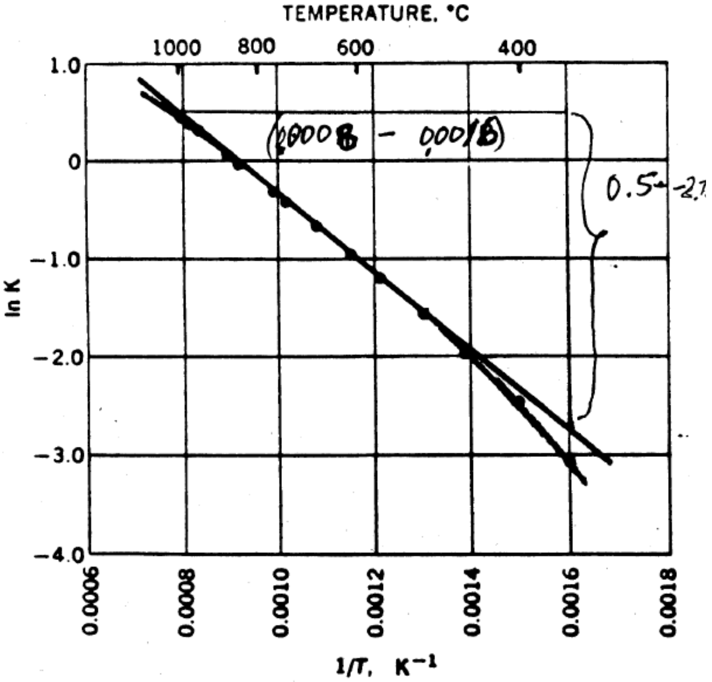
(b) For the all-gas reaction $CO_2 + H_2 = CO + H_2O$ the temperature dependence has been measured.



The temperature dependence of the equilibrium constant for the reaction $CO_2 + H_2 \rightleftarrows CO + H_2O$

Determine $\Delta_{rxn}H^\ominus$ for this reaction at 600 °C. **Describe** the states that this$\Delta_{rxn}H^\ominus$ corresponds to.

Equation	Basis for the equation	Eq. #
$\Delta_{rxn}\mathbf{G}^{\ominus} = - RT \ln K_p$ or $(\Delta_{rxn}\mathbf{G}^{\ominus}/T) = - R\ln K_p$	Derived in lecture notes Part 9	1
$(\partial(\Delta_{rxn}\mathbf{G}^{\ominus}/T)/\partial T)_p$ $= - R\, d(\ln K_p/dT)$	differentiate Eq 1 with respect to T at constant p	2
$(\partial(\Delta_{rxn}\mathbf{G}^{\ominus}/T)/\partial T)_p$ $= - \Delta_{rxn}\mathbf{H}^{\ominus}/T^2$	We derived in the previous problem	3
$- R\, d(\ln K_p/dT)$ $= - \Delta_{rxn}\mathbf{H}^{\ominus}/T^2$	Combine Eq 2 & 3	4
$d \ln K_p =$ $(-\Delta_{rxn}\mathbf{H}^{\ominus}/R)d(1/T)$ This states that $- \Delta_{rxn}\mathbf{H}^{\ominus}/R$ at temperature T_1 is the slope of the tangent to the $\ln K_p$ vs $(1/T)$ curve at that temperature	From Eq 4	5

From the given plot of ln K_p vs 1/T we find the slope at 600 °C: slope =(0.50 - -2.75)K /(0.0008 - 0.0016) = - 4062.5 K		6
- $\Delta_{rxn}\mathbf{H}^{\ominus}/R$ at 600 °C = - 4062.5 K $\Delta_{rxn}\mathbf{H}^{\ominus}$ = 4062.5 K •8.31451J $K^{-1}mol^{-1}$ $\Delta_{rxn}\mathbf{H}^{\ominus}$ = 33778. J mol^{-1} **Answer**	From Eq 5 This corresponds to gases, $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ behaving ideally in the limit p → 0.	7