Statistical Molecular Thermodynamics

Christopher J. Cramer

Video 12.6

Temperature Dependence of *K*

Dependence of K on T

We can apply the Gibbs-Helmholtz equation (cf. video 8.7)

$$\left(\frac{\partial \Delta G^\circ / T}{\partial T}\right)_P = -\frac{\Delta H^\circ}{T^2}$$

And substitute $\Delta_r G^\circ(T) = -RT \ln K_P(T)$

$$\boxed{\left(\frac{\partial \ln K_P(T)}{\partial T}\right)_P = \frac{d \ln K_P(T)}{dT} = \frac{\Delta_r H^\circ}{RT^2}}$$

van't Hoff Equation

- Endothermic: $\Delta_r H^\circ > 0$ $K_P(T)$ increases with T.
- Exothermic: $\Delta_r H^\circ < 0$ $K_P(T)$ decreases with T.

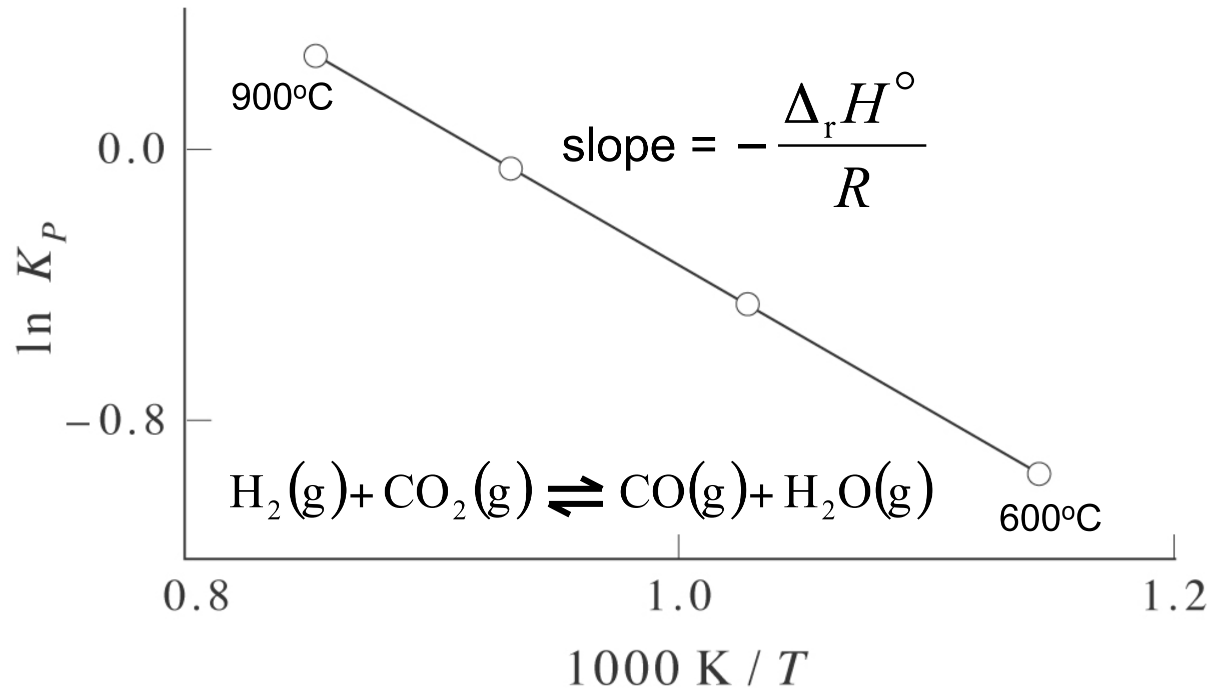
Another manifestation of Le Châtelier's principle

Integrating the van't Hoff Equation

$$\frac{d\ln K_P(T)}{dT} = \frac{\Delta_r H^\circ}{RT^2} \xrightarrow{\text{integrate}} \ln\frac{K_P(T_2)}{K_P(T_1)} = \int_{T_1}^{T_2} \frac{\Delta_r H^\circ(T)}{RT^2}\,dT$$

Over small T ranges we can consider $\Delta_r H^\circ$ constant (T independent):

$$\ln\frac{K_P(T_2)}{K_P(T_1)} = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$



Clausius-Clapeyron analog

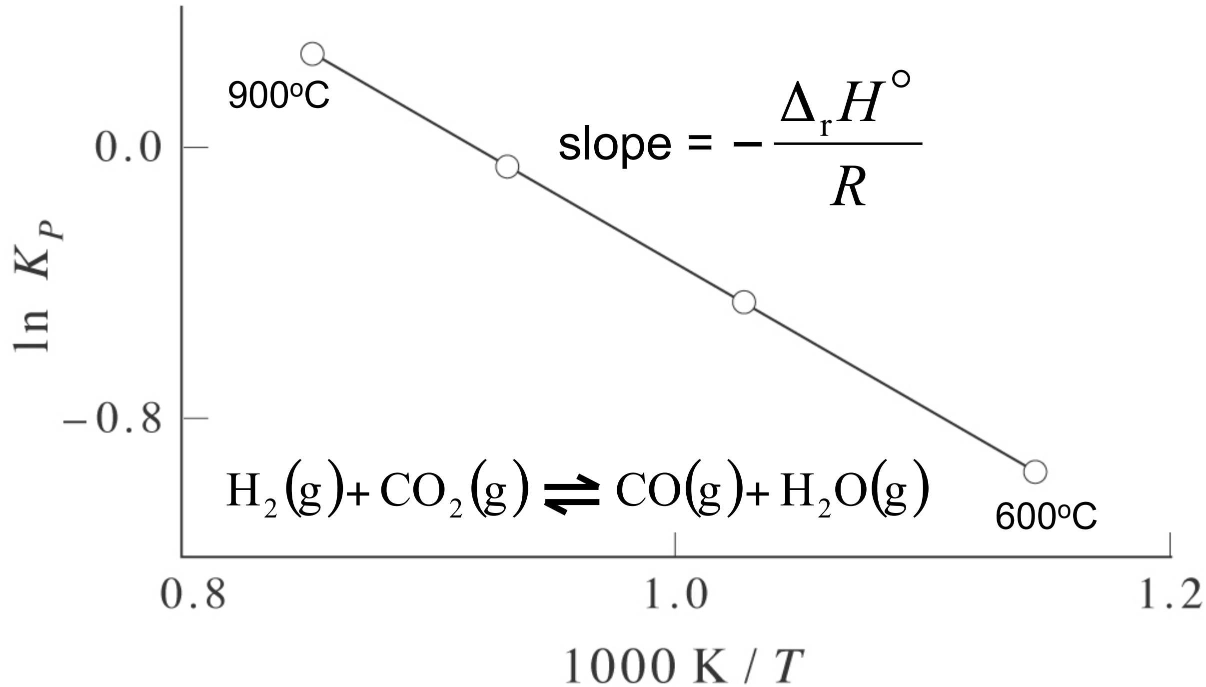
$$X(g) \rightleftharpoons X(l)$$

$$\ln\frac{P_2}{P_1} = -\frac{\Delta_{vap}\bar{H}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

(cf. video 9.6)

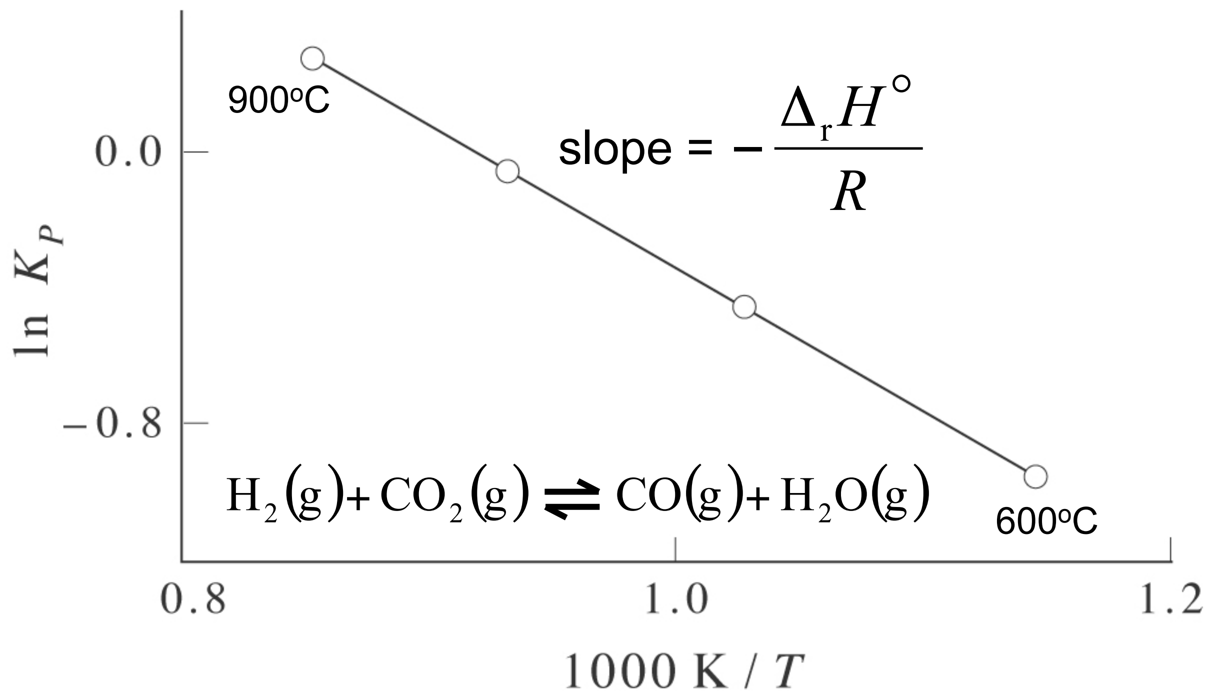
Self-assessment

Is the water gas shift reaction as written below exothermic or endothermic?



Self-assessment Explained

Is the water gas shift reaction as written below exothermic or endothermic?



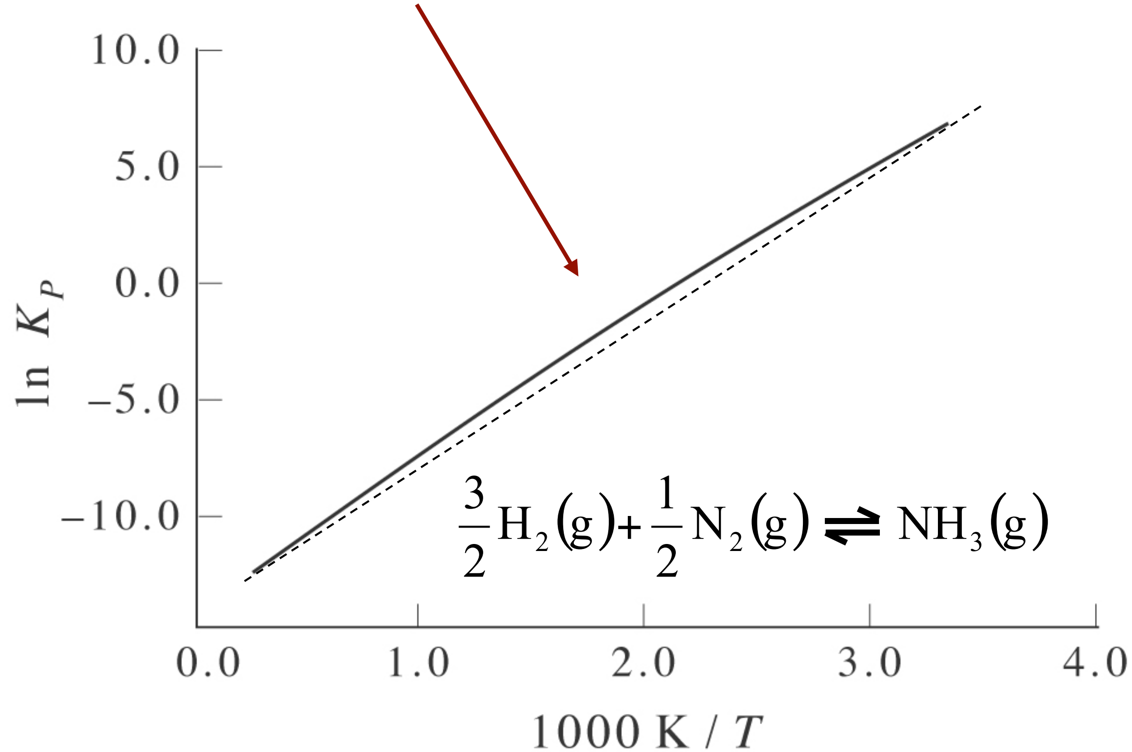
<u>Endothermic</u>. One can see this either by noting that K_P is larger at higher temperature, or by noting that the slope being negative implies $\Delta_r H^o$ must be positive.

Integrating the van't Hoff Equation

If we *cannot* consider $\Delta_r H(T)$ constant over the T range,

$$\ln \frac{K_P(T_2)}{K_P(T_1)} = \int_{T_1}^{T_2} \frac{\Delta_r H^\circ(T)}{RT^2} dT \longrightarrow \ln K_P(T) = \ln K_P(T_1) + \int_{T_1}^{T} \frac{\Delta_r H^\circ(T')}{RT'^2} dT'$$

the van't Hoff plot is no longer linear



We do know how to calculate the T dependence of ΔH,

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} C_P^\circ(T) dT$$

where $C_P(T)$ is often reported as a series in T from an experimental fit,

$$C_P^\circ(T) = A + BT + CT^2 + \cdots$$

Next: Determining K from Q (the other Q)