STATISTICAL MOLECULAR THERMODYNAMICS

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Video 8.7

P and *T* Dependence of *G*

PRESSURE DEPENDENCE OF *G*

We know already (see Video 8.4): $\left(\dfrac{\partial G}{\partial P}\right)_T = V$

integrating $\Delta G = \int_{P_1}^{P_2} V dP \quad (\text{constant } T)$

For 1 mole of ideal gas: $\Delta \overline{G}(T) = RT \int_{P_1}^{P_2} \frac{1}{P} dP = RT \ln \frac{P_2}{P_1}$

If $P_1 = 1 \text{ bar}, P_2 = P$: $\Delta \overline{G}(T) = \overline{G}(T,P) - \overline{G}(T, 1 \text{ bar}) = RT \ln \frac{P}{1 \text{ bar}}$

Rearranged: $\overline{G}(T,P) = \underline{G°(T)} + \underline{RT \ln P}$

The *standard molar Gibbs free energy*. One mole of ideal gas at one bar. Depends on T alone.

adjustment to P from one bar.

TEMPERATURE DEPENDENCE OF G

$$G = H - TS \xrightarrow{\text{divide by } T} \frac{G}{T} = \frac{H}{T} - S$$

Differentiate wrt T at constant P:

$$\left[\frac{\partial(G/T)}{\partial T}\right]_P = -\frac{H}{T^2} + \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P$$

$$= -\frac{H}{T^2} + \frac{C_P}{T} - \frac{C_P}{T}$$

video 7.1

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

The Gibbs-Helmholtz equation

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

e.g., for a reaction

TEMPERATURE DEPENDENCE OF *G*

As we know how to determine $H(T)$ and $S(T)$ individually, we can also use,

$$\overline{G}(T) = \overline{H}(T) - T\overline{S}(T)$$

Using $H(0)$ as the reference for enthalpy/free energy,

$$\overline{G}(T) - \overline{H}(0) = \underline{\overline{H}(T) - \overline{H}(0)} - T\underline{\overline{S}(T)}$$

$$\begin{aligned} H(T) - H(0) = &\int_0^{T_{\mathrm{fus}}} C_P^{\mathrm{s}}(T)\,dT + \Delta_{\mathrm{fus}}H \\ &+ \int_{T_{\mathrm{fus}}}^{T_{\mathrm{vap}}} C_P^{\mathrm{l}}(T)\,dT + \Delta_{\mathrm{vap}}H \\ &+ \int_{T_{\mathrm{vap}}}^{T} C_P^{\mathrm{g}}(T)\,dT \end{aligned}$$

(see video 5.8)

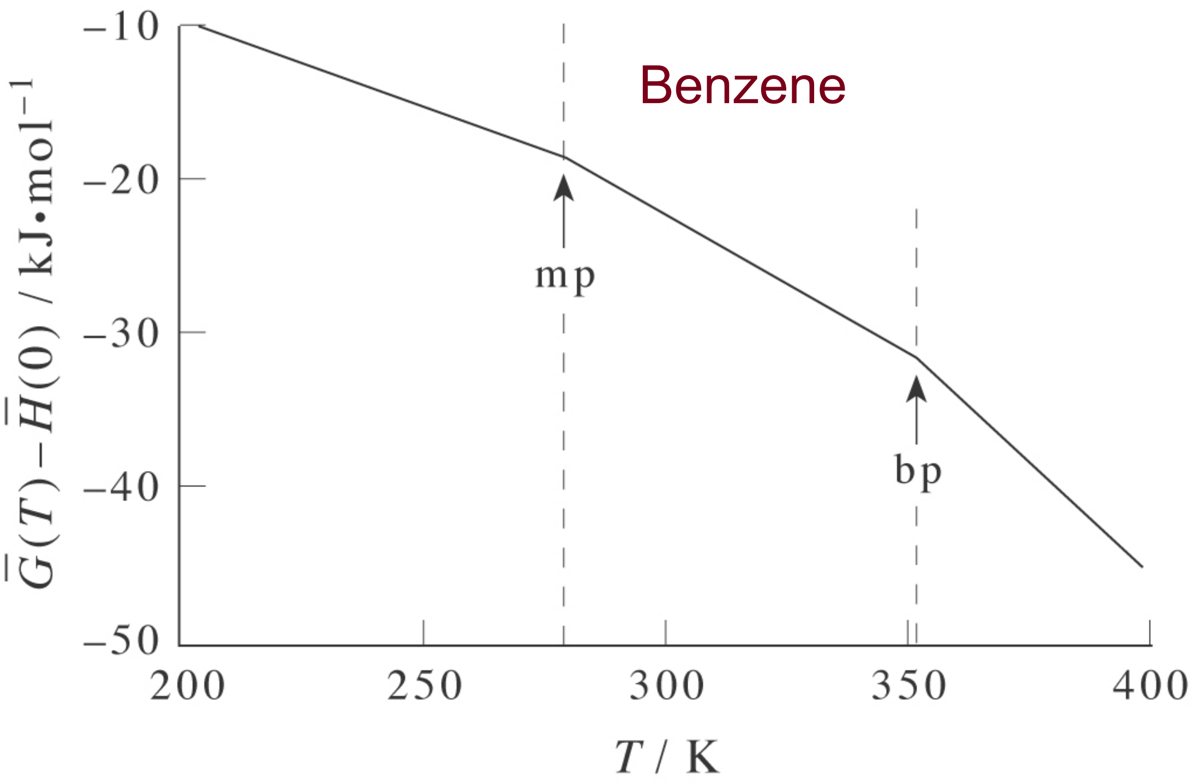
$$\begin{aligned} S(T) = &\int_0^{T_{\mathrm{fus}}} \frac{C_P^{\mathrm{s}}(T)}{T}\,dT + \frac{\Delta_{\mathrm{fus}}H}{T_{\mathrm{fus}}} \\ &+ \int_{T_{\mathrm{fus}}}^{T_{\mathrm{vap}}} \frac{C_P^{\mathrm{l}}(T)}{T}\,dT + \frac{\Delta_{\mathrm{vap}}H}{T_{\mathrm{vap}}} \\ &+ \int_{T_{\mathrm{vap}}}^{T} \frac{C_P^{\mathrm{g}}(T')}{T'}\,dT' \end{aligned}$$

(see video 7.3)

BENZENE EXAMPLE: *G* AT 1 BAR

$$dG = -SdT + VdP$$

G decreases with increasing *T*



$$\bar{G}(T)-\bar{H}(0)=\bar{H}(T)-\bar{H}(0)-T\bar{S}(T)$$

Continuous at phase transitions since equilibrium implies same *G*

$$\Delta_{\mathrm{trs}}G = 0$$

Discontinuous *slope* at phase transitions

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$S(\mathrm{g}) > S(\mathrm{l}) > S(\mathrm{s})$$