Statements of the third law

- **The Gibbs-Helmholtz equation:**

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P$$

- **For an isothermal process:**

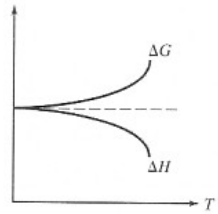
$$\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P$$

- **These equations imply:**

$$\lim_{T\to 0}\Delta G = \lim_{T\to 0}\Delta H$$

Statements of the third law

$$\lim_{T\to 0}\Delta G = \lim_{T\to 0}\Delta H$$

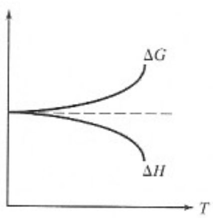


- **Nernst postulated the following:**

$$\lim_{T\to 0}\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = 0, \qquad \lim_{T\to 0}\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = 0$$

Statements of the third law

$$\lim_{T\to 0}\Delta G = \lim_{T\to 0}\Delta H$$

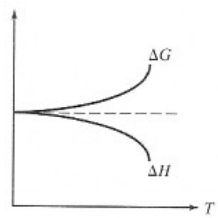


- **Nernst postulate implies that:**

$$\lim_{T\to 0}\left[\frac{\partial(G_2 - G_1)}{\partial T}\right]_P = \lim_{T\to 0}\left[\frac{\partial G_2}{\partial T} - \frac{\partial G_1}{\partial T}\right] = \lim_{T\to 0}\left[S_1 - S_2\right] = 0$$

Statements of the third law

$$\lim_{T\to 0}\Delta G = \lim_{T\to 0}\Delta H$$

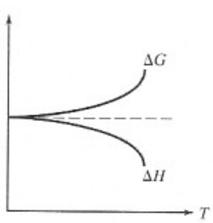


- **The Nernst formulation of the Third Law:**

'All reactions in a liquid or solid in thermal equilibrium take place with no change of entropy in the neighborhood of absolute zero.'

Statements of the third law

$$\lim_{T\to 0}\Delta G = \lim_{T\to 0}\Delta H$$

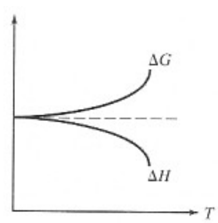


- **Planck later postulated that:**

$$\lim_{T\to 0}\left(\frac{\partial G}{\partial T}\right)_P = 0, \quad \lim_{T\to 0}\left(\frac{\partial H}{\partial T}\right)_P = 0 \quad \Rightarrow \quad \lim_{T\to 0} S = 0$$

Statements of the third law

$$\lim_{T\to 0}\Delta G = \lim_{T\to 0}\Delta H$$

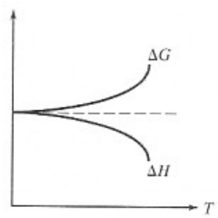


- **Planck's statement of the Third Law:**

'The entropy of all systems in internal equilibrium is the same at absolute zero, and may be taken to be zero.'

Statements of the third law

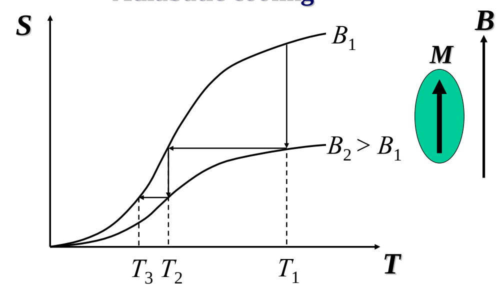
$$\lim_{T\to 0}\Delta G = \lim_{T\to 0}\Delta H$$



- **Another statement of the Third Law is:**

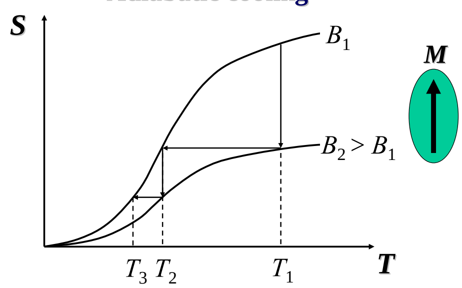
'It is impossible to reduce the temperature of a system to absolute zero using a finite number of processes.'

Adiabatic cooling



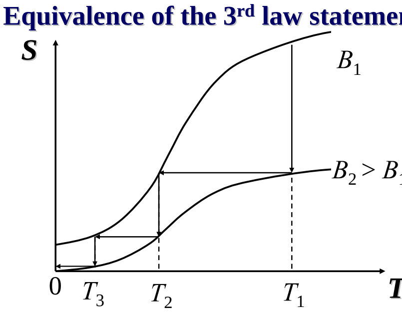
$$dU = TdS - PdV = TdS - MdB = đQ - MdB$$

Adiabatic cooling



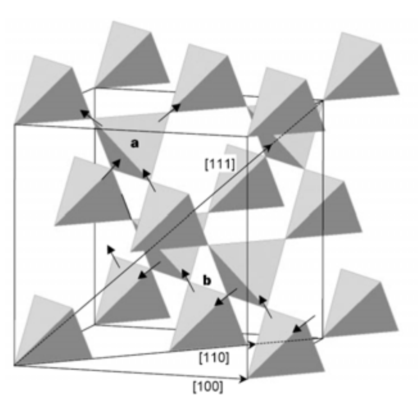
$$dU = TdS - PdV = TdS - MdB = đQ - MdB$$

Equivalence of the 3rd law statements



$$dU = TdS - PdV = TdS - MdB = đQ - MdB$$

Ice violates the Planck 3rd Law



$$\lim_{T\to 0} C_p = \lim_{T\to 0} C_V = 0$$

$$\lim_{T\to 0}\left(\frac{\partial S}{\partial p}\right)_T = 0$$

$$\Rightarrow \lim_{T\to 0}\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \lim_{T\to 0}\beta_p = 0$$