

# Properties of Gibbs energy

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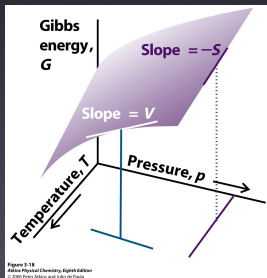
# $G$ increases with $P$ and decreases with $T$

If  $G(P, T)$ , then

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$$

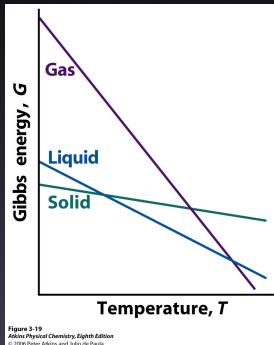
Compare with  $dG = VdP - SdT$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \text{ and } \left(\frac{\partial G}{\partial T}\right)_P = -S$$



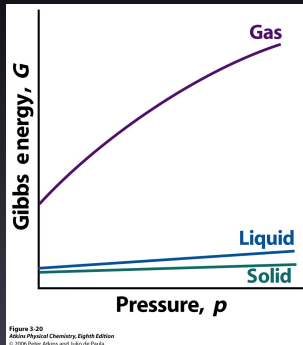
Both  $V$  and  $S$  are always positive.  
 $G$  increases as  $P$  increases  
 $G$  decreases as  $T$  increases.

# Variation of $G$ with $T$ for different phases



Lowest slope for solid  
Highest slope for gas  
Liquid intermediate

# Variation with $P$ of $G$



Slope small for sol. and liq.

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

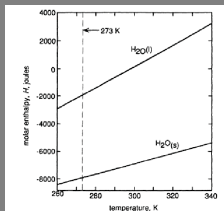
At constant  $T$ ,

$$\int dG = V \int dP$$

High slope for gas

# G variation with $T$ from $H$ and $S$

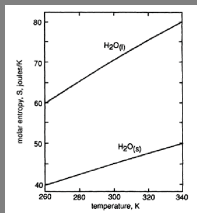
## $H$ variation



$$H_m(T) = H_m(T_0) + \int_{T_0}^T C_P dT$$

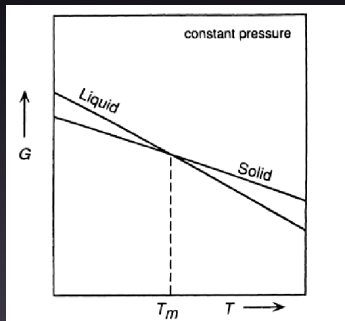
## $S$ variation

$$S_m(T) = S_m(T_0) + \int_{T_0}^T \frac{C_P}{T} dT$$



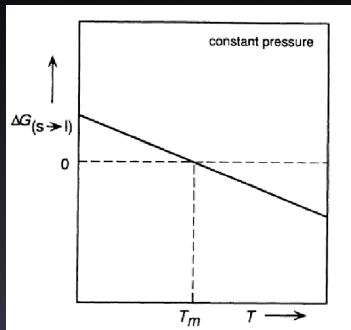
Compute Gibbs energies per mole of liquid and solid water

$$G_m(T) = H_m(T) - TS_m(T)$$



Less than  $T_m$ ,  $G_m$  of solid is less than liquid. Above  $T_m$ ,  $G_m$  liquid is less than solid.

# Criterion of spontaneity



$\Delta G_m(s \rightarrow l)$  is  $> 0$  above the melting point,  $T_m$ , and  $< 0$  below. From the condition  $(dG)_{T,P} \leq 0$ , we see that at  $T_m$  solid and liquid are in equilibrium and below  $T_m$  solid is stable.