

Physical Chemistry lecture

2.5.



Part 2.5. Criteria for the spontaneity of physicochemical processes

2.5.1. Spontaneity and equilibrium

2.5.2. Meaning and concept of free enthalpy

2.5.3. Meaning and concept of free energy

2.5.4. Calculation of enthalpy changes and free energies

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What about the thermodynamic incentives for this reaction?

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incentives = structural & energetic

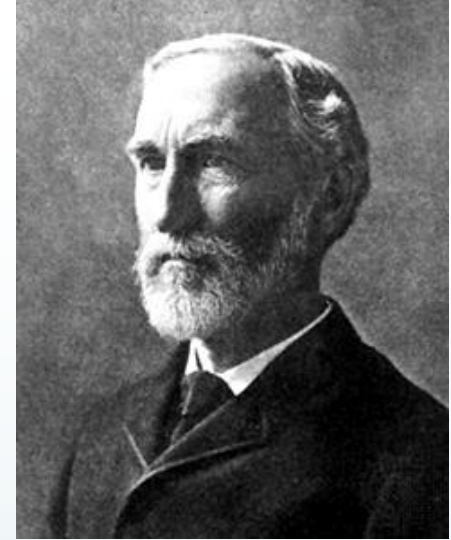


Free enthalpy (Gibb's free energy)

2.5.3

$$G \equiv H - TS$$

Gibbs free energy is extremely useful, especially in describing chemical and biochemical processes, because most of them take place under isothermal-isobaric conditions.



In isothermal-isobaric conditions it is a direct measure of the spontaneity of processes.

The value of changes in free enthalpy can be calculated for any process, not necessarily isothermal-isobaric, but only in such conditions does it have a simple physical meaning "free" means reduced by the value of volumetric work

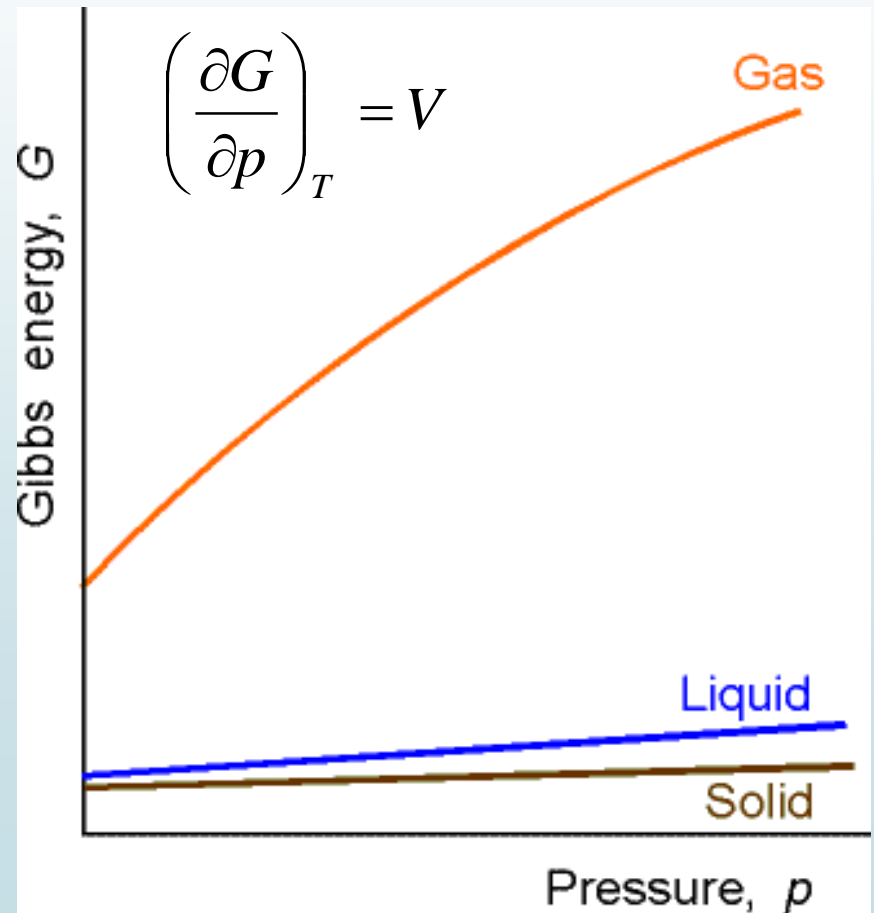
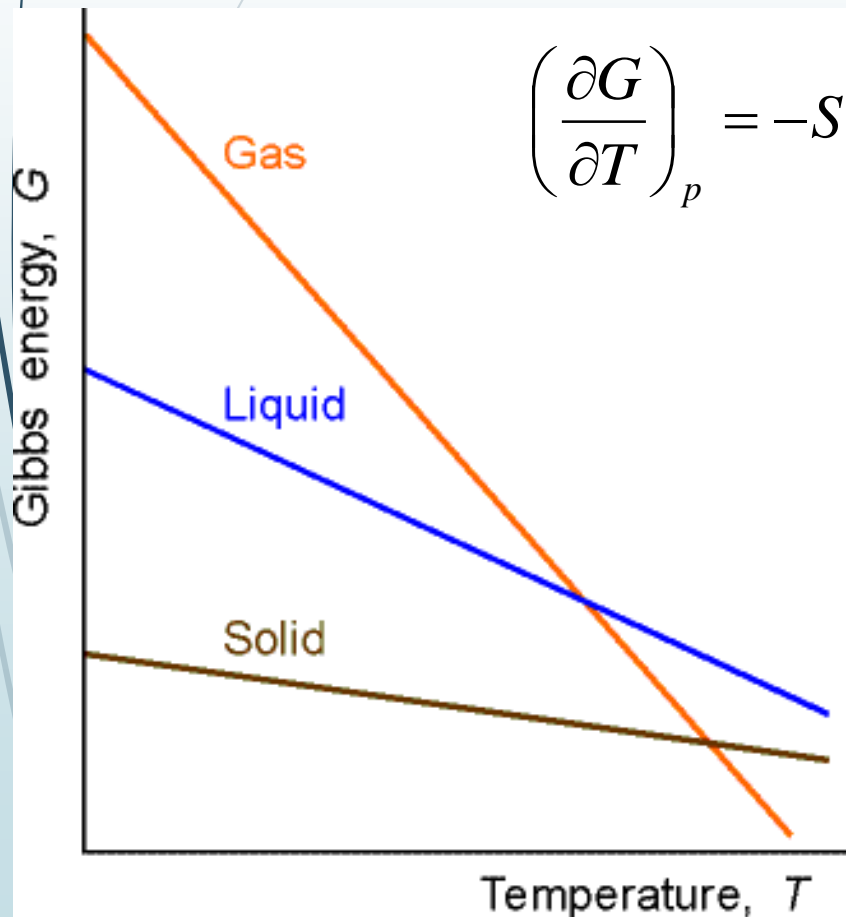
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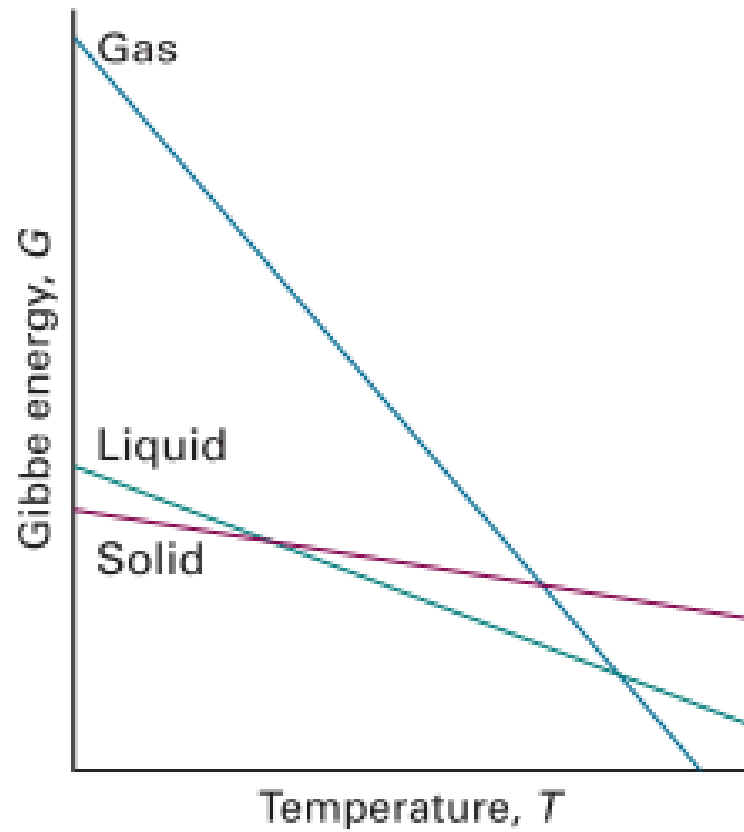
$$d_i S \stackrel{def}{=} dS - \frac{Q_{el}}{T} \geq 0$$

2.5.4

$$G \equiv H - TS$$

Free enthalpy depends on both the thermodynamic parameters and the type of substance.





Gibb's free Energy & Helmholtz's free energy

2.5.6

def

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$dH = Q_{el} + Vdp \quad Q_{el} = TdS$$

$$dG = -SdT + Vdp$$

$$dG = \left(\frac{\partial G}{\partial T} \right)_p dT + \left(\frac{\partial G}{\partial p} \right)_T dp$$

$$\left(\frac{\partial G}{\partial p} \right)_T = V \quad \left(\frac{\partial G}{\partial T} \right)_p = -S$$

def

$$F = U - TS$$

$$dF = dU - TdS - SdT$$

$$dU = Q_{el} - pdV$$

$$dF = -SdT + pdV$$

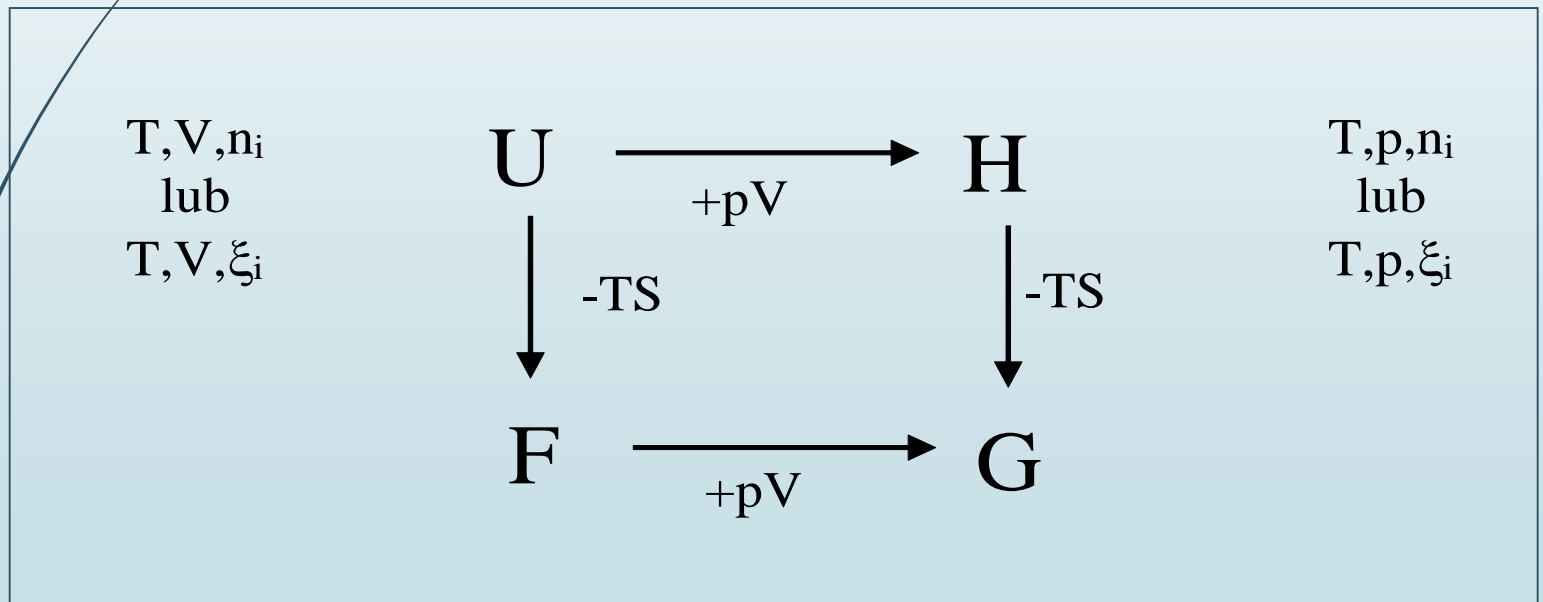
$$dF = \left(\frac{\partial F}{\partial T} \right)_V dT + \left(\frac{\partial F}{\partial V} \right)_T dV$$

$$\left(\frac{\partial F}{\partial T} \right)_V = -S \quad \left(\frac{\partial F}{\partial V} \right)_T = -p$$

Gibb's free Energy & Helmholtz's free energy

$$F \stackrel{\text{def}}{=} U - TS$$

$$G \stackrel{\text{def}}{=} H - TS$$



Thermodynamic potentials

$$dG = -SdT + Vdp + \overline{W}_{el}$$

$$dF = -SdT - pdV + \overline{W}_{el}$$

$$dU = TdS - pdV + \overline{W}_{el}$$

$$dH = TdS + Vdp + \overline{W}_{el}$$

CONDITIONS OF EQUILIBRIUM AND SPONGEINITY OF PROCESSES

2.5.9

isothermal-isobaric

isothermal-isochoric

$$\begin{cases} dG = \overline{W}_{el} \\ dG < \overline{W}_{el} \end{cases}$$

$$\begin{cases} dF = \overline{W}_{el} \\ dF < \overline{W}_{el} \end{cases}$$

$$\overline{W}_{el} = 0$$

$$\begin{cases} dG = 0 \\ dG < 0 \end{cases}$$

$$\begin{cases} dF = 0 \\ dF < 0 \end{cases}$$

$$dG = dH - TdS$$

Samorzutność procesu i towarzyszące mu zmiany funkcji termodynamicznych

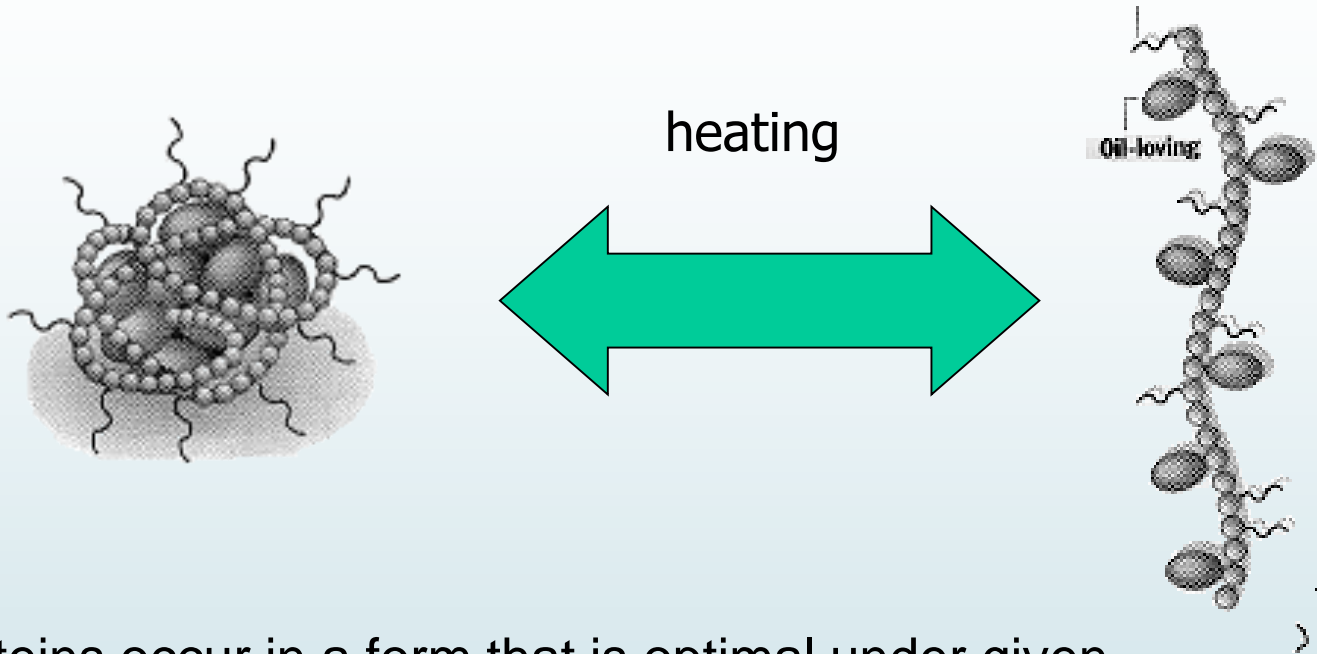
Czynnik entalpowy ΔH	Czynnik entropowy ΔS	Zmiana entalpii swobodnej ΔG	Temperatura	Proces
$\Delta H < 0$	$\Delta S > 0$	dla każdego ΔH i ΔS $\Delta G < 0$	dowolna	samorzutny – zachodzi dzięki zmianie entropii i entalpii we wszystkich temperaturach
$\Delta H < 0$	$\Delta S < 0$	$\Delta H > T\Delta S$ $\Delta G < 0$	niska	samorzutny tylko w niskich temperaturach – uwarunkowany wyłącznie zmianą entalpii
		$\Delta G > 0$	wysoka	niesamorzutny
$\Delta H > 0$	$\Delta S > 0$	$\Delta G > 0$	niska	niesamorzutny
		$\Delta H < T\Delta S$ $\Delta G < 0$	wysoka	samorzutny tylko w wysokich temperaturach – uwarunkowany wyłącznie zmianą entropii
$\Delta H > 0$	$\Delta S < 0$	$\Delta G > 0$	dowolna	niesamorzutny – niezależnie od temperatury



Example

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Thermodynamic analysis of protein denaturation



- proteins occur in a form that is optimal under given conditions – native state (or cluster of states)- protein denaturation can occur under the influence of heat or chemical factors (including detergents, salts, heavy metal ions, pH)- during denaturation, non-covalent interactions are weakened (Coulomb, van der-Waals, dipole, hydrogen bonds, solvation, etc.).

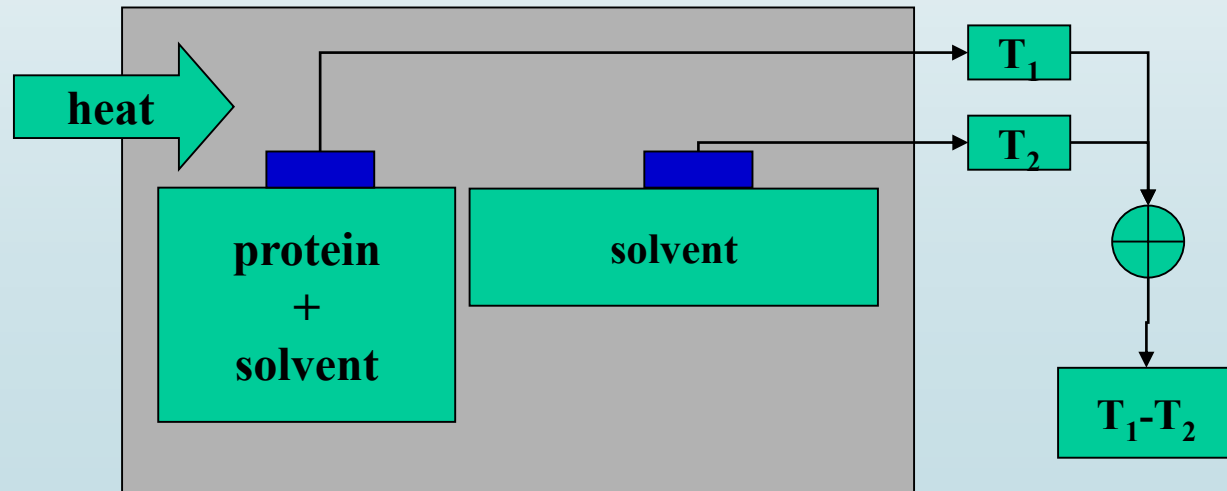
Data for lysozyme

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	10°C	25°C	60°C	100°C
ΔG° kJ/mol	67.4	60.7	27.8	-41.4
ΔH° kJ/mol	137	236	469	732
ΔS° J/ K mol	297	586	1318	2067
$T\Delta S^\circ$ kJ/mol	69.9	175	439	771

At what temperature does denaturation occur?

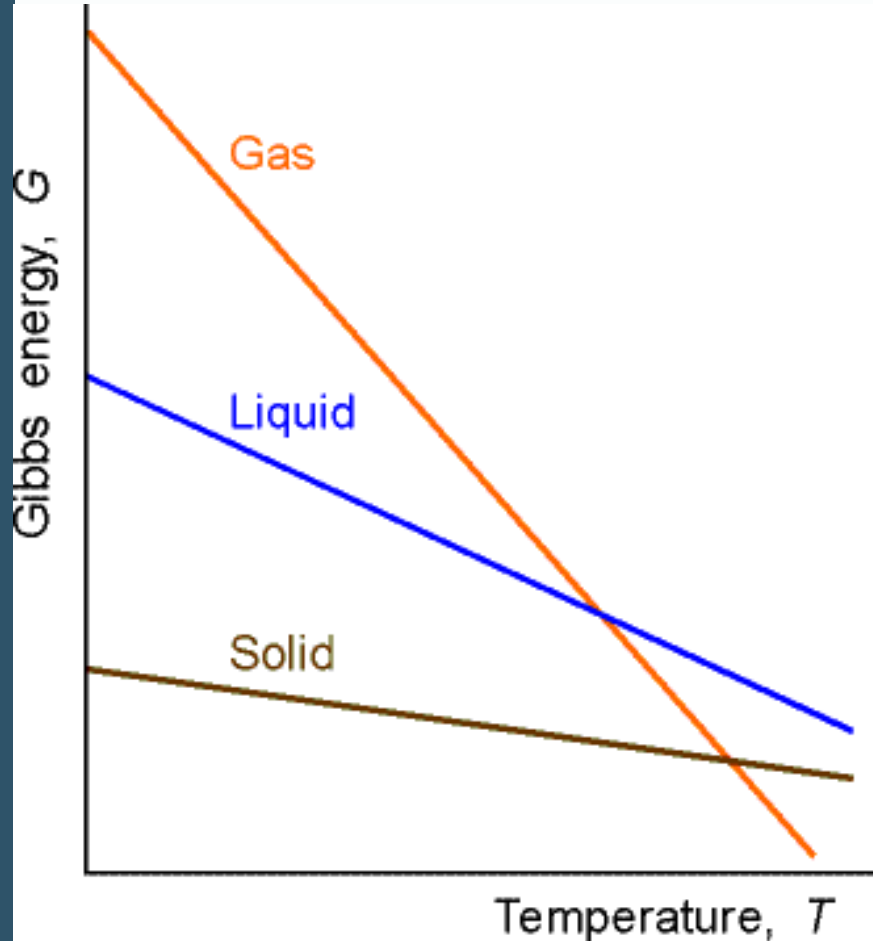
Protein Thermal Denaturation Measurement



Measurement of temperature differences due to heating. This is essentially a measurement of the heat capacity of a system.

TEMPERATURE DEPENDENCE OF GIBBS'S FREE ENERGY

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The changes in free enthalpy due to temperature are mainly determined by entropy, because substances in different states of matter differ significantly.

$$\Delta G = \Delta H - T\Delta S$$

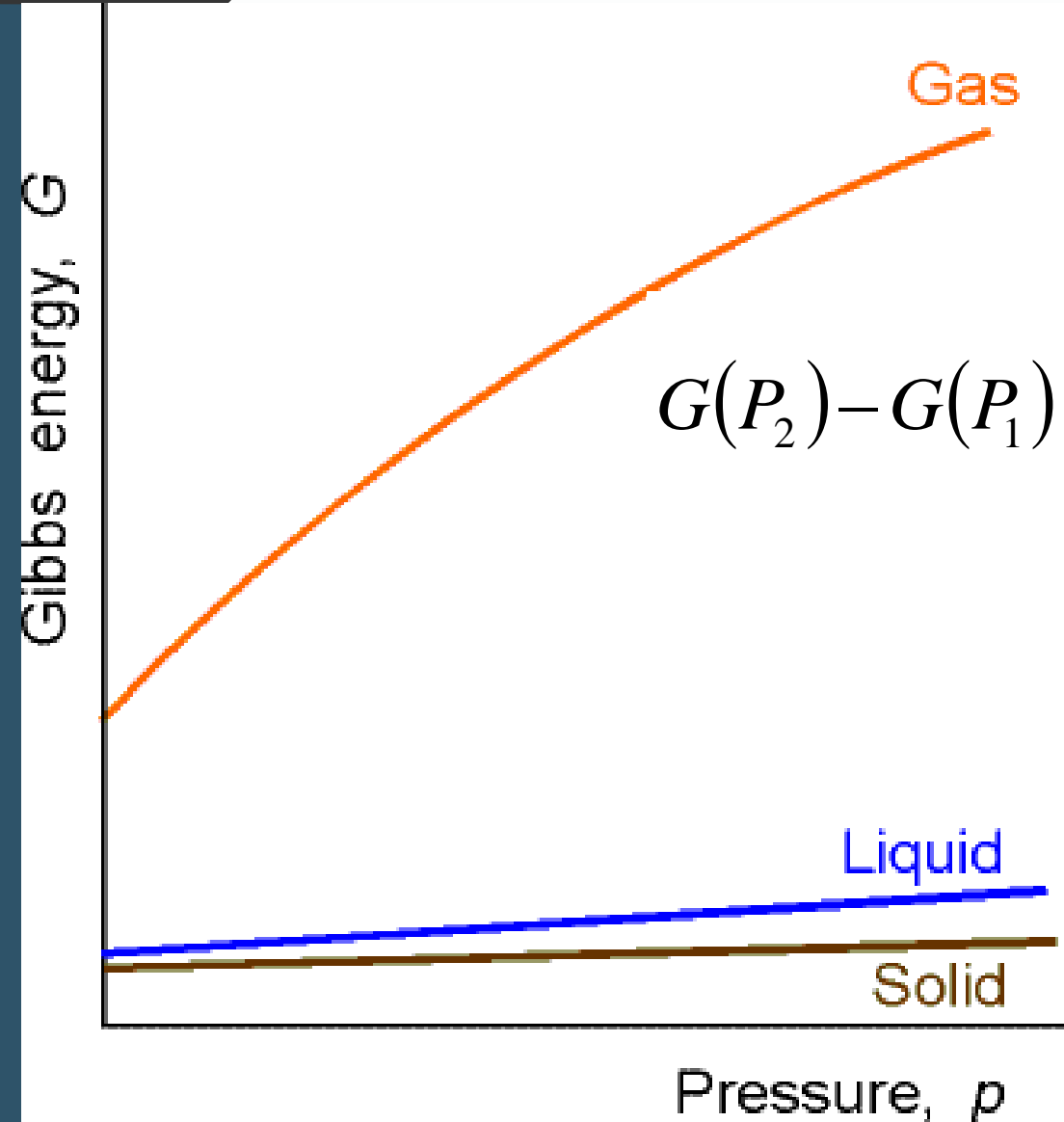
The change in temperature has the greatest influence on the change in free enthalpy for gaseous substances and the smallest for solids.

$$\Delta G(T_1) = \Delta G(298) - \int_{298}^T \Delta S(T) dT$$
$$\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} = - \int_{T_1}^{T_2} \frac{\Delta H(T)}{T^2} dT$$

PRESSURE DEPENDENCE OF GIBBS'S FREE ENERGY

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$$dG = -SdT + Vdp + \overline{W}_{el}$$



$$G(P_2) - G(P_1) = \int_{P_1}^{P_2} \frac{nRT}{P} dP = nRT \ln \left(\frac{P_2}{P_1} \right)$$

The change in volume has the greatest influence on the change in free enthalpy for gaseous substances and the least for solids.

Is it possible to convert graphite into diamond by increasing pressure? If so, what is the minimum pressure?

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$$dG = -SdT + Vdp + \overline{W}_{el}$$

Approximate solution: $\Delta G = \int dG = \int Vdp \cong \Delta(Vp)$

$$G(P_2) - G(P_1) = (V_2 \cdot P_2 - V_1 \cdot P_1)$$

Experimental data: $\overline{V}_{graphite} = 5.33 \text{ cm}^3 / \text{mol}$

$$\overline{V}_{diamond} = 3.42 \text{ cm}^3 / \text{mol}$$

$$\Delta G(P) = \Delta G(1 \text{ atm}) + \Delta V \cdot (P - 1)$$

$$\Delta G(P) = 2.84 - 1.935 \cdot 10^{-4} \cdot (P - 1)$$

We are looking for the pressure value for which there will be at least a state of equilibrium between allotropic forms of carbon.

$$\Delta G = 0$$

$$0 = 2.84 - 1.935 \cdot 10^{-4} (P - 1) \text{ kJ/mol}$$

$$P = 15,000 \text{ atm}$$

In practice, the pressure must be even higher.