



Chemical Thermodynamics & Equilibrium

Session Slides with Notes

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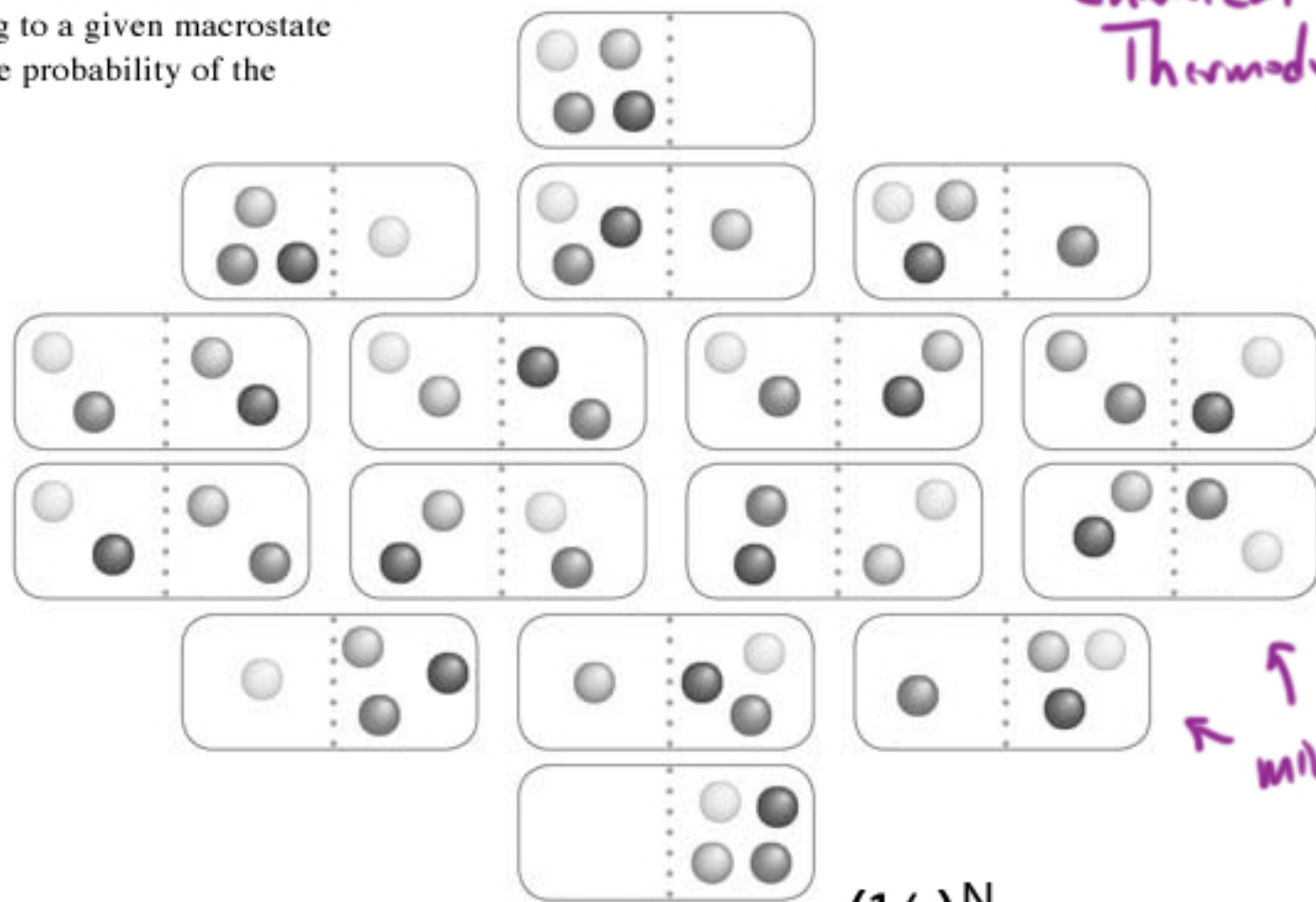


The entropy of the world
only increases.

It never decreases.

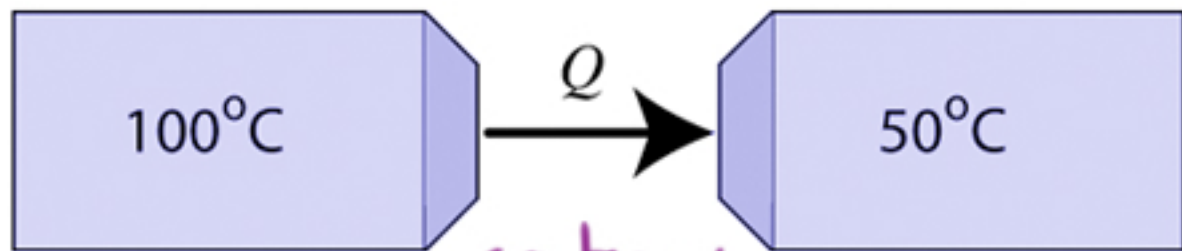
The greater the number of microstates corresponding to a given macrostate the greater the probability of the macrostate.

Chemical
Thermodynamics



↑
↑
↖ microstates

probability of all particles being in half the container $(1/2)^N$



$$\Delta S_H = \frac{Q}{T_H}$$

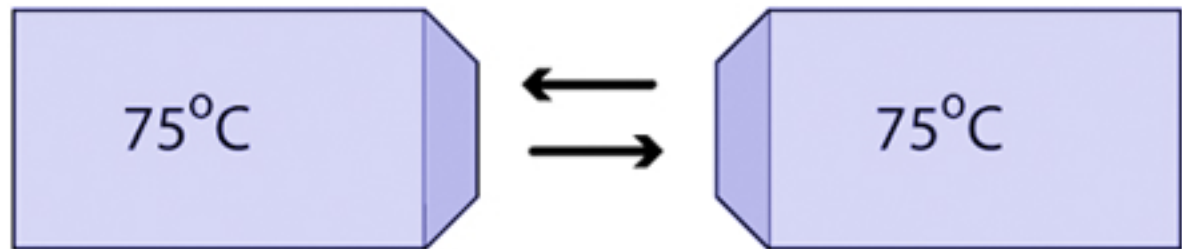
spontaneous

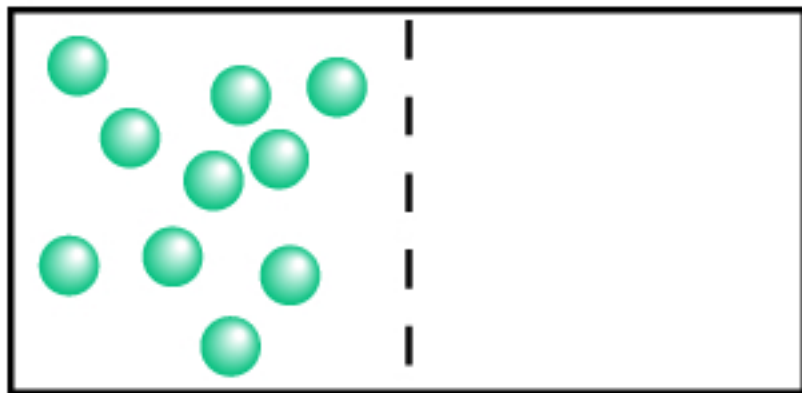
$$\Delta S_C = \frac{Q}{T_C}$$

(simplified)

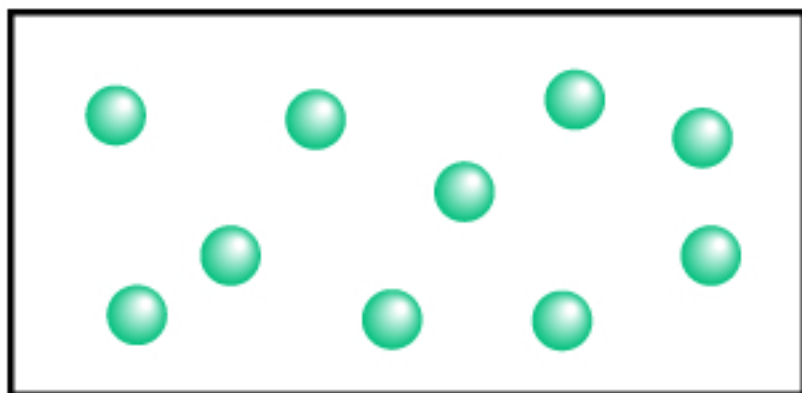
$$\Delta S = \frac{Q}{T}$$

$$\Delta S_{\text{universe}} \oplus$$

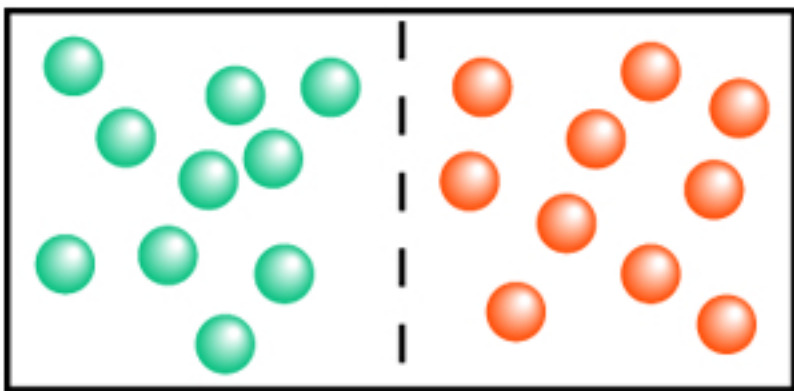




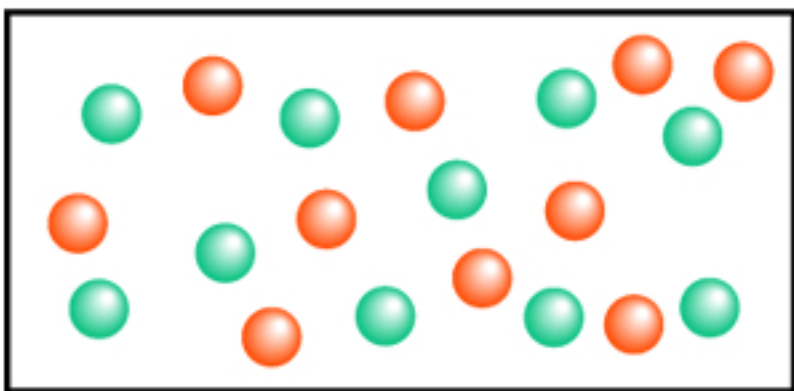
ΔS_{system} is \oplus



$\Delta S_{\text{universe}}$ is also \oplus

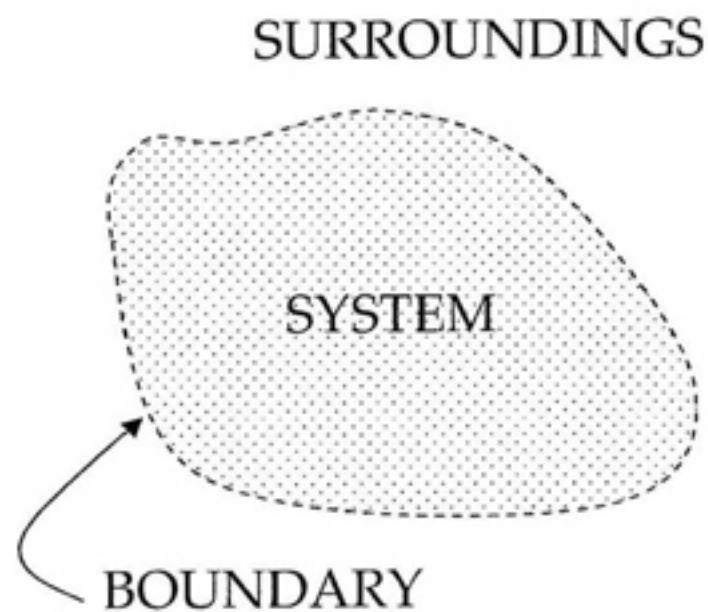


entropy of
mixture



$\Delta S_{\text{system}} \oplus$

$$\Delta S_{\text{world}} = \Delta S_{\text{system}} + \Delta S_{\text{environment}}$$



$$\Delta S_{\text{environment}} = \frac{Q_{\text{environment}}}{T}$$

$\Delta S_{\text{surroundings}}$ is because of heat flow

UNIVERSE = system + surroundings

$$G = H - TS$$

← Entropy of the system

A state function that when it changes means the entropy of the universe changed.

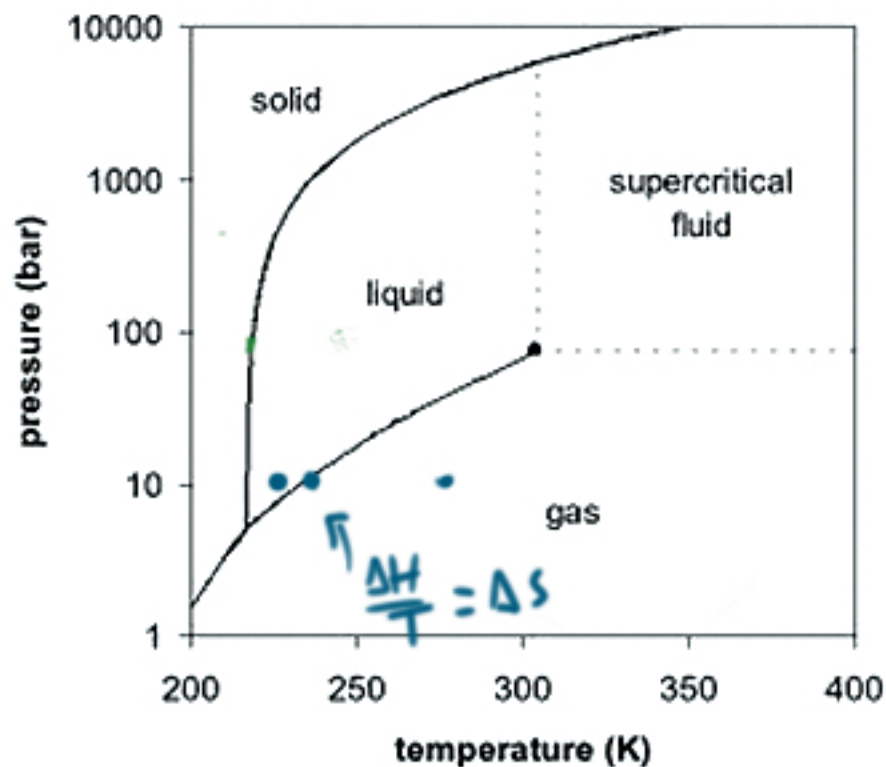
$$\Delta G = \Delta H - T \Delta S$$

$$\text{When } \Delta G = 0$$

$$\frac{-\Delta G}{T} = \frac{-\Delta H}{T} + \Delta S$$

↑ $\Delta S_{\text{universe}}$ ↑ $\Delta S_{\text{surroundings}}$ ↑ ΔS_{system}

$$\frac{\Delta H}{T} = \Delta S_{\text{system}}$$



10 bar 225 K

gas \rightarrow liquid

$$G_{\text{gas}} > G_{\text{liquid}}$$

10 bar 275 K

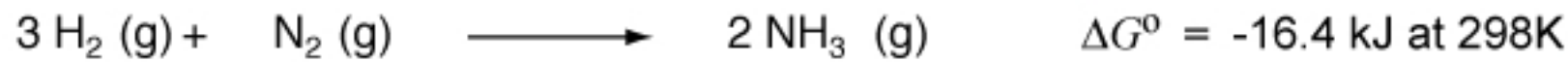
liquid \rightarrow gas

$$G_{\text{liquid}} > G_{\text{gas}}$$

$$-\frac{\Delta G}{T} = -\frac{\Delta H}{T} + \Delta S$$

\uparrow favors liquid \uparrow favors gas

$$Q = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3 [\text{N}_2]}$$



standard free energy change

ΔG° describes $[A] = [B]$
 $\uparrow \quad \rightarrow$
 IM



$$Q = \frac{[B]}{[A]}$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$K_{eq} = e^{\left(\frac{-\Delta G^\circ}{RT}\right)}$$

$$\Delta G = \Delta G^\circ + 2.3RT \log Q$$

$Q \rightarrow K \Leftrightarrow \Delta G \rightarrow 0$

$$\Delta G^\circ = -2.3RT \log K$$

with all $[\text{NH}_3]$
and no $[\text{H}_2][\text{N}_2]$

$$K = e^{-\Delta G^\circ / RT}$$

IF ΔG° is \ominus
 K is a big #
 IF ΔG° is \oplus
 K is a fraction

Which of the following statements about the relationship between ΔG° , the standard free energy change, and K , the thermodynamic equilibrium constant, is untrue?

- A. If ΔG_0 is large and positive, K is very small.
- B. If ΔG_0 is large and negative, K is very large.
- C. If ΔG_0 is zero, $K = 1$.
- D.** All of the above are true.

Which of the following is the proper expression of K_c for the following reaction?



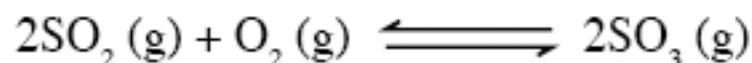
A. $\frac{[\text{NH}_3][\text{O}_2]}{[\text{NO}][\text{H}_2\text{O}]}$

B. $\frac{4[\text{NO}]6[\text{H}_2\text{O}]}{4[\text{NH}_3]5[\text{O}_2]}$

C. $\frac{[\text{NO}]^4[\text{H}_2\text{O}]^6}{[\text{NH}_3]^4[\text{O}_2]^5}$

D. $\frac{[\text{NH}_3]^4[\text{O}_2]^5}{[\text{NO}]^4[\text{H}_2\text{O}]^6}$

The equilibrium constant under standard conditions for the reaction of SO_2 with O_2 to form SO_3 , $K_c = 1.5 \times 10^{-1}$



If 0.01 mol of each of the three gases are present along with argon in a 1 liter container at STP, which of the following is occurring?

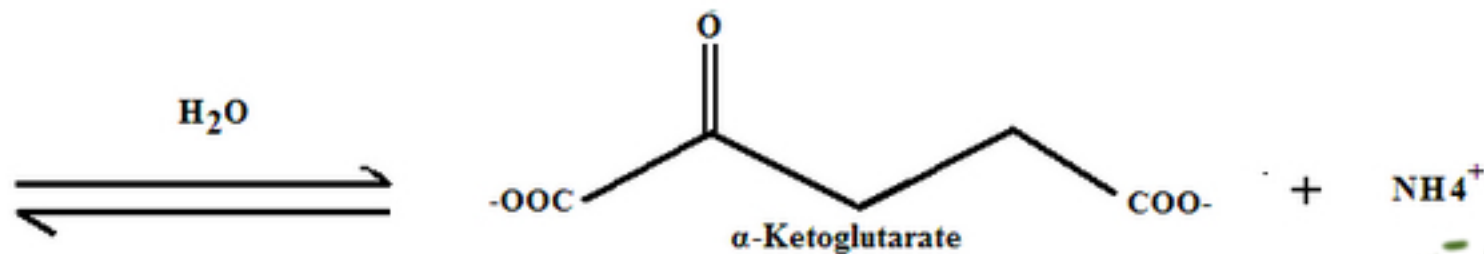
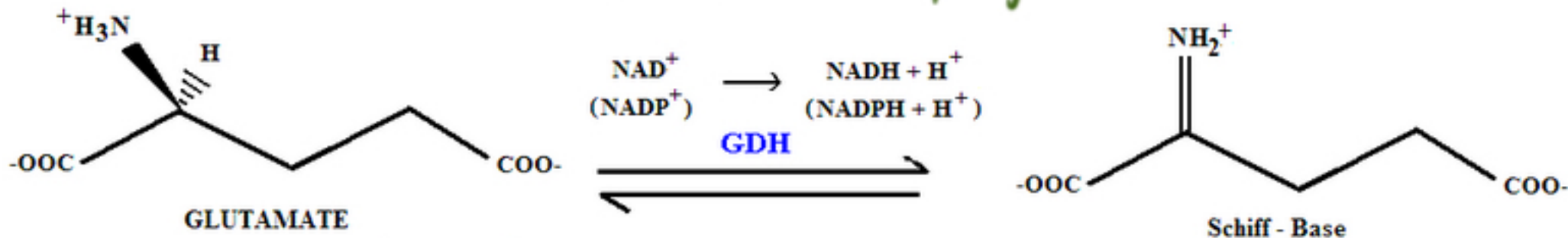
- A. The forward reaction occurs at a higher rate than the reverse reaction.
- B. The reverse reaction occurs at a higher rate than the forward reaction.
- C. The reaction is at equilibrium.
- D. Pressure is increasing in the container.

$$Q = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$$

$$= \frac{(0.01)^2}{(0.01)^2 (0.01)}$$

$$Q = 100$$

Glutamate Dehydrogenase

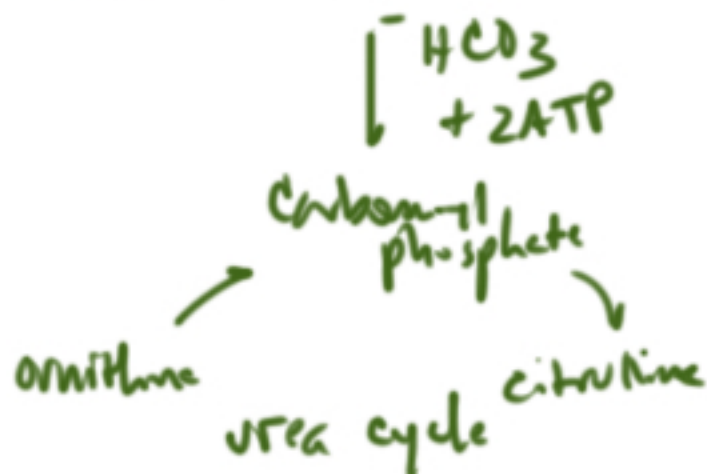


product removal

ΔG° is somewhat \oplus

However $[\text{NH}_4^+]$ is kept very low.

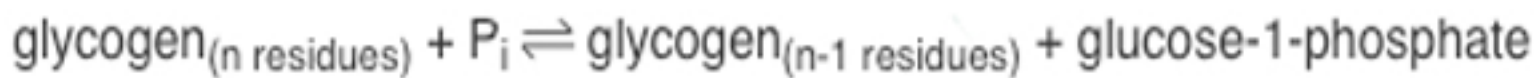
$$\Delta G = \Delta G^\circ + RT \ln Q$$



storage
of glucose
↓

Glycogen Phosphorylase

product
removal
↓



in liver
and
muscle

ΔG° is actually \oplus

However

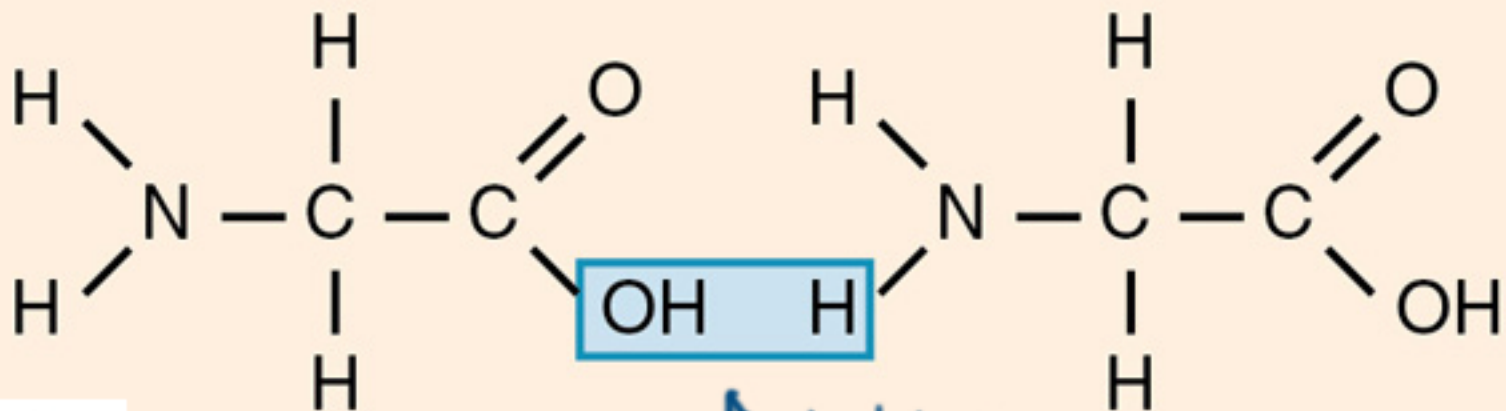
in physiology

$$\frac{[G1P]}{[P_i]} \sim \frac{1}{1000}$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

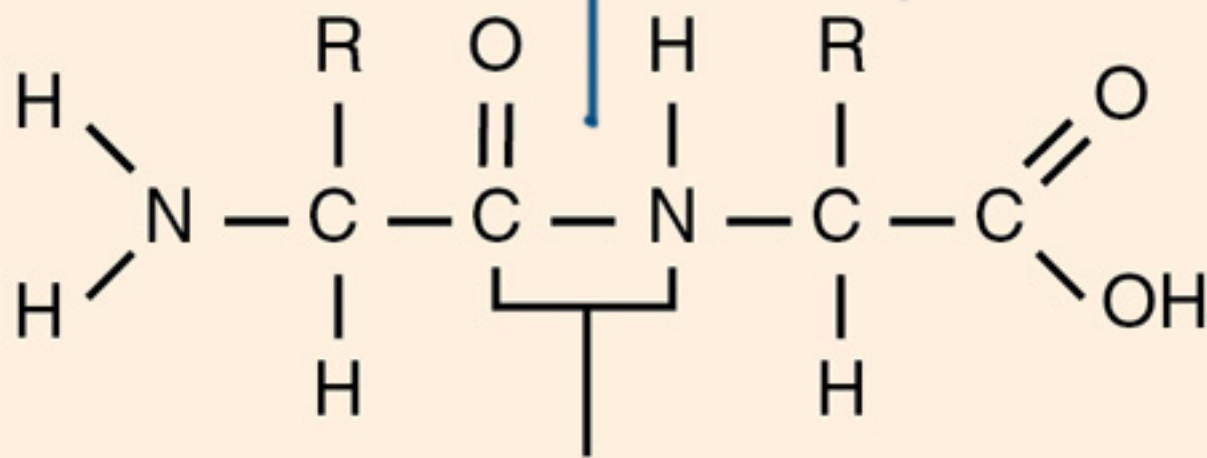
↓ phosphogluco
mutase
glucose-6
phosphate

↓ glucose-6
phosphatase
glucose



While not thermodynamically stable, proteins are kinetically stable.

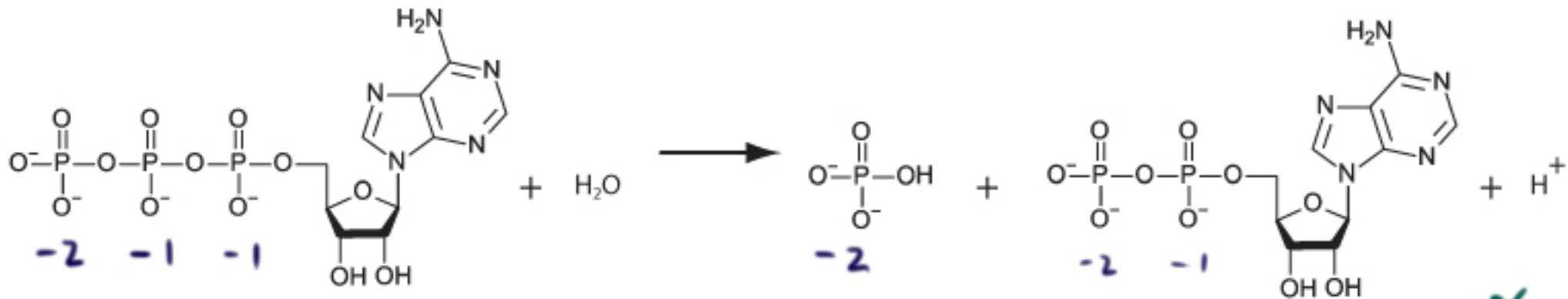
hydrolysis is spontaneous



Peptide Bond

Hydrolysis of ATP

$$\Delta G^\circ \sim -30 \text{ kJ}$$



$$u_e = \frac{u_{g, g_2}}{r}$$



$$\Delta U \text{ is } \ominus$$

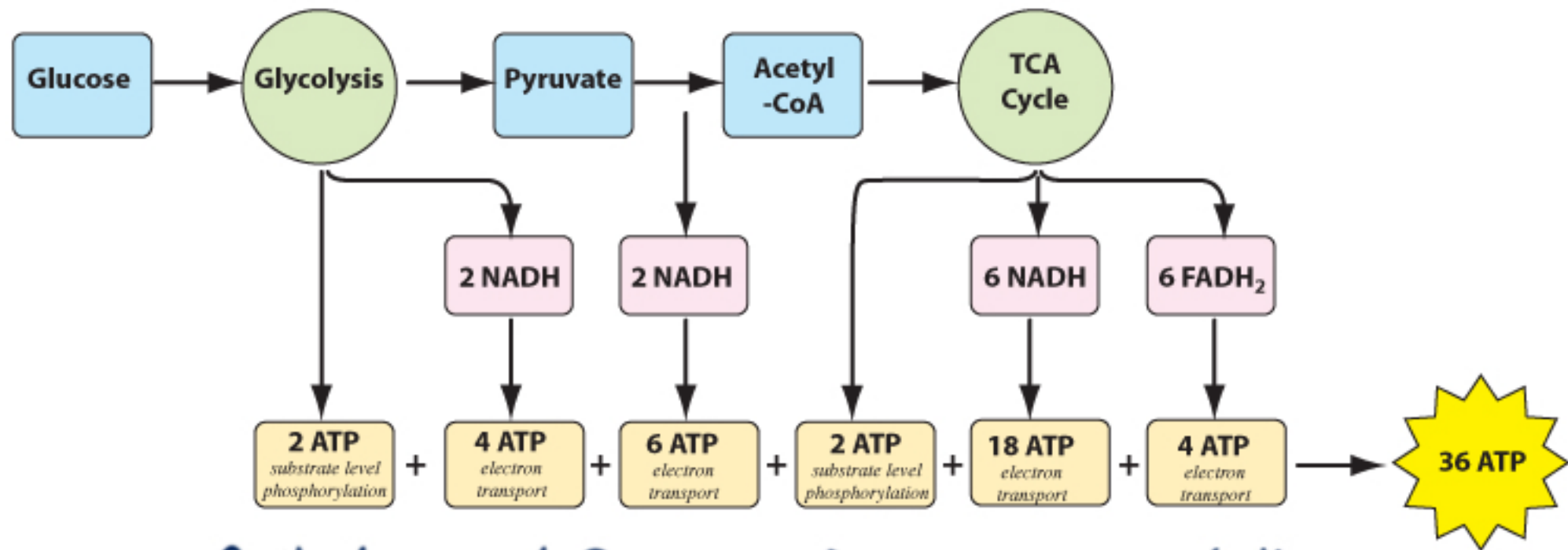
$$\Delta H \text{ is } \ominus$$

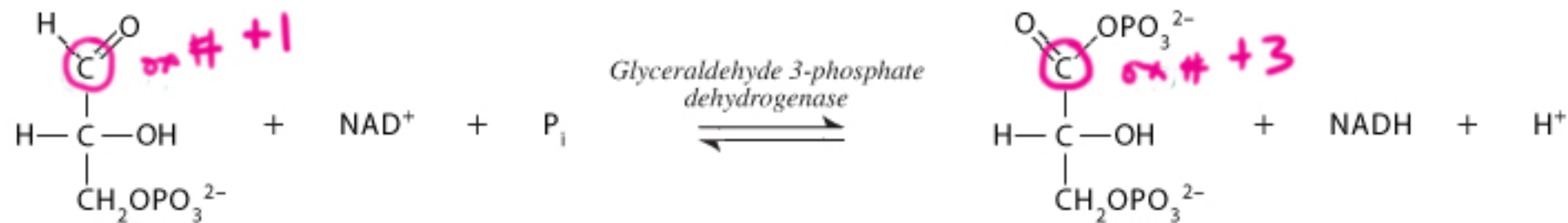
$$\Delta G \text{ is } \ominus$$

$$K = e^{-\Delta G^\circ / RT}$$

with ATP

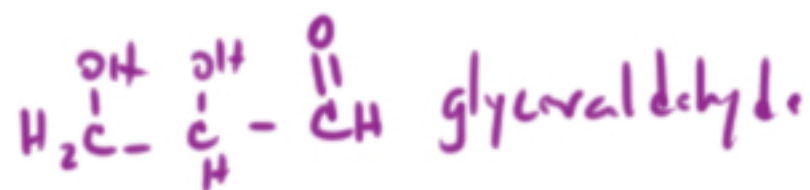
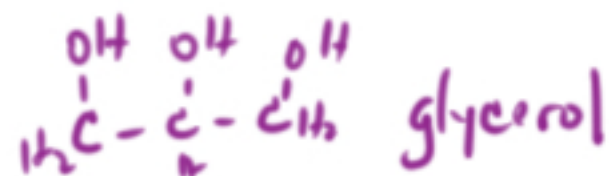
$$K = e^{(-\Delta G_a^\circ + \Delta G^\circ) / RT}$$



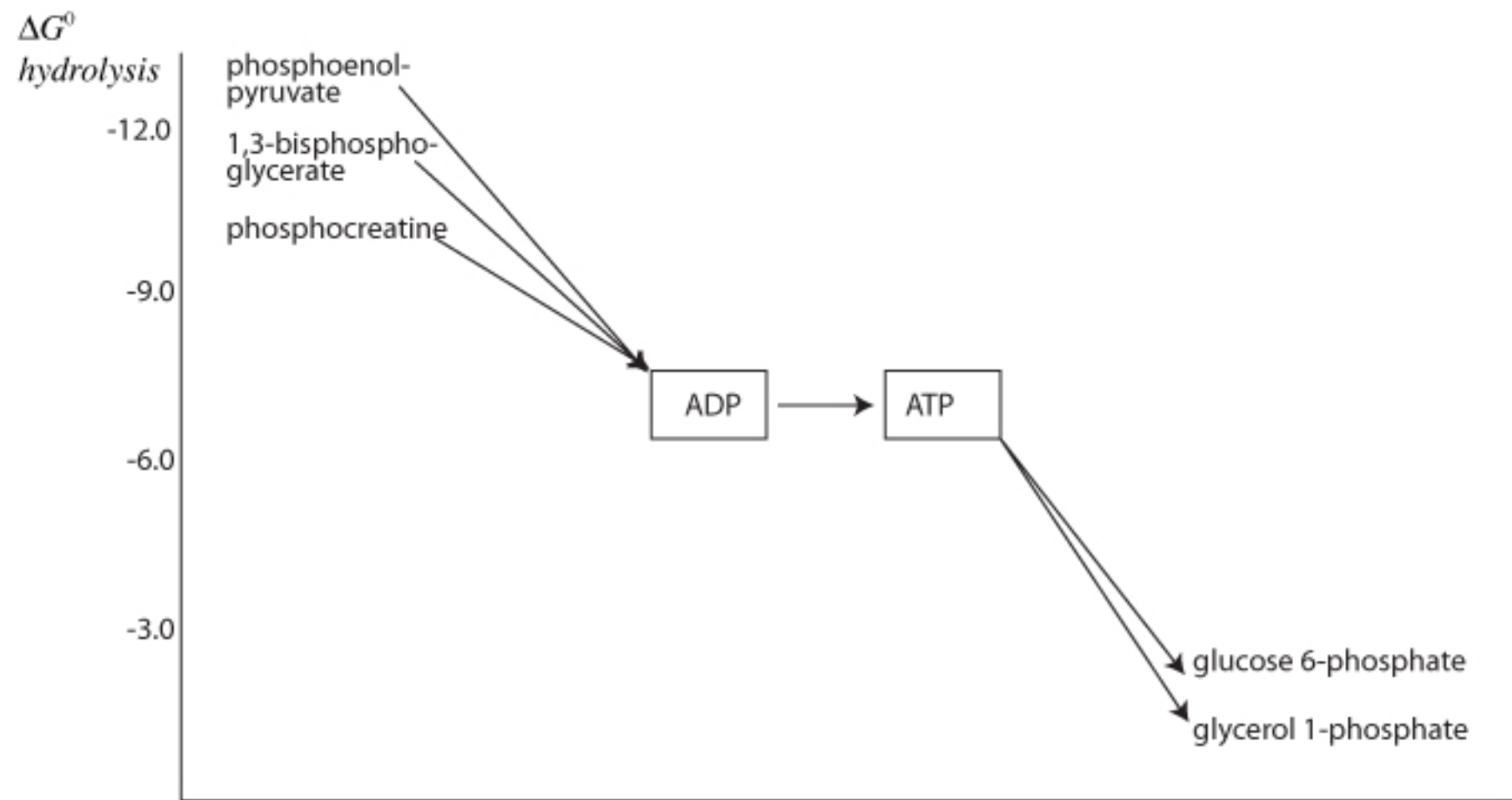


G3P

1,3 BPG



$\Delta G \sim 0$





$$\Delta H^\circ = -46.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = -389 \text{ J K}^{-1} \text{ mol}^{-1}$$

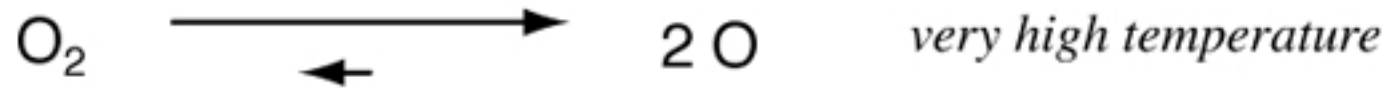
exothermic reaction

$$\Delta G^\circ = -16.4 \text{ kJ at 298K}$$

increasing T favors endothermic direction

$$\ln \frac{K_1}{K_2} = \left(- \frac{\Delta H^\circ}{R} \right) \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

if exothermic this would be \oplus
if $T_2 > T_1$ then this will be \oplus
then $K_1 > K_2$ reaction shifted to favor reactants

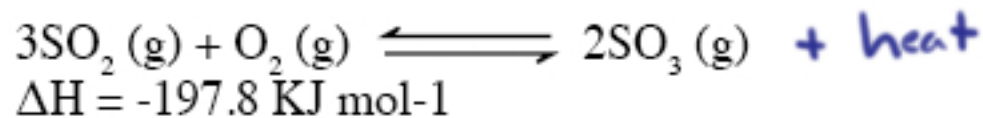


Le Chatelier

If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, then the equilibrium shifts to counter-act the imposed change.

- Concentration - adding reagent or removing product drives a reaction forward
- Temperature - Increasing T favors the endothermic direction.
$$\text{heat} + A \rightleftharpoons B$$
- Pressure - Increasing P favors the smaller volume (fewer moles of gas)

The reaction of sulfur dioxide with oxygen is as follows:



At 1000°C and 0.3 atm , the equilibrium constant, K_p , is equal to 3.42 . Which of the following strategies would increase the yield of sulfur trioxide?

↑
equilibrium

- I. Increasing the pressure of the reaction vessel
 - II. Introducing a catalyst
 - III. Heating the reaction vessel further
-
- A. I
 - B. I and III
 - C. II and III
 - D. I, II and III

