Thermodynamics

Chem 36

Spring 2002

Thermodynamics

- The study of *energy changes* which accompany physical and chemical processes

Why do we care?

-will a reaction proceed spontaneously?

-if so, to what extent?

It **won't** tell us:

-how *fast* the reaction will occur

-the *mechanism* by which the reaction will occur

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What is Energy? (review!)

- Energy is the ***capacity to do work or to transfer heat***

-**Kinetic Energy**: energy associated with mass in motion (recall: $E_k = \frac{1}{2}mv^2$)

-**Potential Energy:** energy associated with the *position* of an object relative to other objects (energy that is *stored* - can be converted to kinetic energy)

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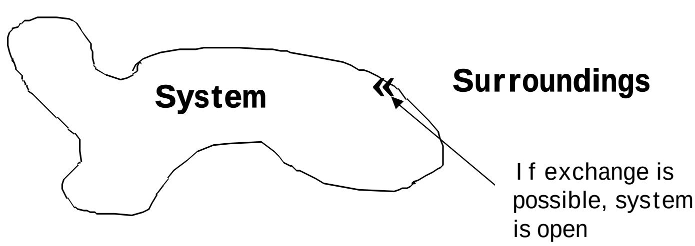
The System *(review)*

- We must define what we are studying:



System: portion of the universe under study

Surroundings: everything else

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First Law of Thermodynamics *(review)*

- "The total energy of the universe is *constant*."
- "Energy is neither created or destroyed in a process, only converted to another form."

  -**Conservation of Energy**
- "*You can't win . . . you can only break even.*"

$$\Delta E = q + w$$

Change in energy of the system

(state function)

Heat Flow:

+ is **into system**

- is out of system

(path function)

Work: + is done **on system**

- is done **by system**

(path function)

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Enthalpy *(review)*

- Chemistry is commonly performed at *constant pressure*, so:

  -it is easy to measure *heat flow* (q_p)

  -work ($P\Delta V$) is small (but finite) and hard to measure

Define a new term: **Enthalpy (H)**

$$H = E + PV$$

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Relating Enthalpy and Heat *(review)*

- Recall: $\mathbf{DE = q + w}$
- At constant pressure: $\mathbf{DE = q_p - PDV}$
- Rearranging: $\mathbf{q_p = DE + DPV}$

  $q_p = D(E + PV)$

- Substituting: $\underline{\boldsymbol{q_p = DH}}$

So, if we measure $\boldsymbol{q_p}$, then we can obtain the enthalpy change (ΔH) directly (Calorimetry!)

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How are ΔE and ΔH related? *(review)*

- From the definition of Enthalpy:

$$\mathbf{DH = DE + PDV}$$

-for an ideal gas: $\mathbf{PDV = RTDn}$

So: $\boxed{\mathbf{DH = DE + RTDn}}$

DH ↑ q_p DE ↑ q_v $RTDn$ ↑ PV work

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ΔH and *Spontaneity*

- Shouldn't ΔH be a good indicator of reaction *spontaneity*?
  - ✓ If ΔH < 0, products at a *lower energy* than reactants

Examples:

CH_4 (g) + $2O_2$ (g) → CO_2 (g) + $2H_2O$ (g) ΔH = -802 kJ

4Fe (s) + $3O_2$ (g) → $2Fe_2O_3$ (s) ΔH = -1648 kJ

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But what about . . .

These are spontaneous processes too:

NaCl (s) → Na^+ (aq) + Cl^- (aq) ΔH = **+**

H_2O (s) → H_2O (l) ΔH = **+**

- Both are *nearly* enthalpy neutral
- Both result in *increased disorder*
- We need another LAW of thermodynamics!

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The 2nd Law of Thermodynamics

- “Spontaneous processes are accompanied by an *increase* in Entropy.”
- “The Entropy of *the Universe* is constantly *increasing.”*

So, what *is Entropy*?

•**Entropy** (S): A measure of the degree of disorder or randomness of a system

•Processes will tend towards conditions with the *highest probability* of occuring

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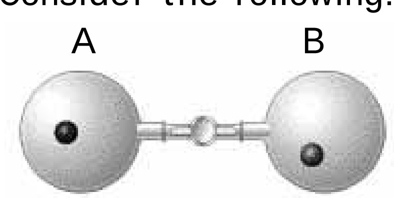
A Little Experiment

Consider the following:



•Two bulbs of equal volume

•Equal number of molecules in each bulb

•*What is the probability of finding ALL of the molecules in Bulb A?*

# molecules	relative probability
1	1/2
2	$1/(2)^2$ (= 1/4)
5	$1/(2)^5$ (= 1/32)
10	$1/(2)^{10}$ (=1/1024)

For 1 mol gas, changing orientations 100 times/sec:

•Event would occur *once* every 10^{14} **years**

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Entropy of Physical States

$S_{solid} < S_{liquid} < S_{gas}$

→ increasing number of possible orientations

So, for a phase change:

Solid → Liquid (spontaneous at $T>T_f$)

Liquid → Gas (spontaneous at $T>T_b$)

$\Delta S > 0$

But, also:

Why spontaneous?

Gas → Liquid (spontaneous at $T<T_b$)

Liquid → Solid (spontaneous at $T<T_f$)

$\Delta S < 0$

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How is Entropy Quantified?

On the *microscopic* level:

$$S = k_B \ln W$$

Boltzmann's constant (= R/N_o)

# of microstates

•Entropy *increases* with an increasing number of microstates (increased "disorder")

•**Units:** $k_b = 1.38 \times 10^{-23}$ J/K (so units of S are: J/K)

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Macroscopic Entropy

- For a *reversible process* at *constant pressure*:

$$\Delta S_{sys} = \frac{q_{p,\,rev}}{T} = \frac{\Delta H}{T_{sys}}$$

•And don't forget:

$$\Delta S_{surr} = - \frac{\Delta H}{T_{surr}}$$

Now, let's revisit the freezing process for water . . .

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Freezing Water: *Revisited*

$H_2O\ (l) \rightarrow H_2O\ (s)$ ΔH = - 6.0 kJ/mol

•Freezing is an *exo*thermic process

•Energy flows from the system to the surroundings:

- •Entropy of the surroundings *increases*
- •Entropy of the system **decreases**

•**Suppose:** $T_{surr} < T_{sys}$ such that T_{surr} is less than FP

- •ΔS_{surr} is ***more positive*** than ΔS_{sys} is negative
- •$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$ = ***positive*** (freezing is spontaneous)

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Quantifying *Spontaneity*

Making some substitutions, we find:

$$\Delta S_{univ} = \Delta S_{sys} - \Delta H / T$$

Re-arranging gives:

$$T\Delta S_{univ} = T\Delta S_{sys} - \Delta H$$

Reversing signs:

$$-T\Delta S_{univ} = \Delta H - T\Delta S_{sys}$$

ΔG (Gibb's Free Energy)

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The Gibbs-Hemholtz Equation

So, at constant temperature and pressure:

DG = DH - TDS

Has units of *Joules* (energy): ***Free* Energy**

•Tells us how much energy is available to do work

All values are for the *system*

What happens at T=0?

We "break even"; *all energy is available to do work.*

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Balancing ΔH and ΔS

Remember: **DG = DH - TDS**

Two considerations:

1. Reactions seek a *minimum* in **Enthalpy** (ΔH)
2. Reactions seek a *maximum* in **Entropy** (ΔS)

-	+	*spontaneous*
+	-	***non**spontaneous*
-	-	*spontaneous at* ***low temps***
+	+	*spontaneous at* **high temps**

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Calculating ΔG for a reaction

ΔG is a *state function*

- Treat like we do ΔH:

DGº = S DGº$_f$ (products) - S DGº$_f$ (reactants)

At 1 atm and 25ºC

Standard Molar Free Energy of Formation: for 1 mol of compound formed from elemental constituents in their standard states

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The 3rd Law of Thermodynamics

We can obtain *absolute* values for Entropy because we have a set reference point:

- If W = 1 (only 1 microstate possible), then S = 0
- So, the <u>3rd Law</u> says:

> "At the *absolute zero of temperature*, the entropy of a perfect crystalline solid is ***zero.***"

So, we can tabulate **S^o** (standard molar entropy) values (NOT ΔS^o) - unlike H and E and G

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Calculating ΔS for a reaction

Entropy is *also* a state function:

DSº = S Sº (products) - S Sº (reactants)

<u>NOTE:</u>

- There are no ΔS^o_f values
- **Sº ¹ 0** for pure elements in their standard states

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Let's Get Quantitative!

Consider the following process:

$$CH_3OH\ (l) \leftrightarrows CH_3OH\ (g)$$

We know:

ΔH^o_{vap} = 38.00 kJ/mol

ΔS^o_{vap} = 112.9 J/K

For most liquids:

$\Delta S^o_{vap} \approx$ 88 J/K
(Trouten's Rule)

At what temperature does methanol boil?

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The BP of Methanol

$$\Delta G^o = \Delta H^o - T\,\Delta S^o$$

- At its BP (T_b), system is at *equilibrium* so ΔG^o=0, and we can write:

$$0 = \Delta H^o_{vap} - T_b\,\Delta S^o_{vap}$$

Rearranging:

$$T_b = \Delta H^o_{vap} / \Delta S^o_{vap}$$

Substituting:

$$T_b = \frac{38.00 \times 10^3\ J}{112.9\ J/K} = \mathbf{336.58\ K} = \boxed{\mathbf{63.4\ ^oC}}$$

Actual BP of Methanol is . . . **64.96 °C**

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There are many paths to ΔG^{o}_{rxn}

- If ΔG^{o}_{f} values are available for products and reactants:

$DG^{o} = S\ DG^{o}_{f}$ (products) - $S\ DG^{o}_{f}$ (reactants)

- If ΔH^{o}_{f} and S^{o} values are available for products and reactants:
  - Calculate ΔH^{o}_{rxn} and ΔS^{o}_{rxn} values
  - **$DG^{o}_{rxn} = DH^{o}_{rxn} - TDS^{o}_{rxn}$**
- Or, use a combination of both methods!

Limits to the utility of ΔG^{o}_{rxn}

- ΔG^{o}_{rxn} predicts reaction spontaneity only when products and reactants are in their *standard states*
- How does ΔG vary with:
  - Pressure (*for gases*)
  - Concentration (*for solutions*)
  - Temperature

Effect of Pressure Change

What happens to *free energy* of a **gas** when we change its pressure?

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

$$G - G^o = 0 - [-nRT\ Ln(P/P^o)]$$

Independent of pressure

It can be derived!

$$\mathbf{G = G^o + nRT\ Ln\ (P/P^o)}$$

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Now, Apply to a Reaction

Let's make some ammonia:

$$N_2\ (g) + 3H_2\ (g) \rightarrow 2NH_3\ (g)$$

For 1 mol of each compound, we can write:

$$G_{NH3} = G^o_{NH3} + RTLn(P_{NH3}/P^o)$$

$$G_{N2} = G^o_{N2} + RTLn(P_{N2}/P^o)$$

$$G_{H2} = G^o_{H2} + RTLn(P_{H2}/P^o)$$

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So, ΔG for the Reaction

Since we know:

$$\Delta G_{rxn} = \Sigma\, \Delta G_{products} - \Sigma\, \Delta G_{reactants}$$

Substituting:

$$\Delta G = 2G_{NH3} - (G_{N2} + 3G_{H2})$$

Finally giving:

$$\Delta G = \Delta G^o + RTLn\left[\frac{(P_{NH3}/P^o)^2}{(P_{N2}/P^o)\,(P_{H2}/P^o)^3}\right]$$

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Some Tweaking

➢ What is P^o?

- P^o = 1 atm (pressure of a gas in its standard state)
- *Numerically*:

$$P_{NH3} = P_{NH3}/P^o$$

Defined as the ***ACTIVITY*** **(= a_{NH3})**

So, now we can write:

$$\Delta G = \Delta G^o + RTLnQ$$

Where:

$$Q = \frac{(a_{NH3})^2}{(a_{N2})\,(a_{H2})^3}$$

Reaction Quotient

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The Reaction Quotient: In General

- For any rection:

$$aA + bB \leftrightarrows cC$$

We can write:

$$Q = \frac{(a_C)^c}{(a_A)^a (a_B)^b}$$

Activity (a) is UNITLESS!

Where, a_X = *activity* of species X

For gases: $a_X = P_x / P^o$ — P^o = 1 atm

For solutions: $a_X = [X] / [X]^o$ — $[X]^o$ = 1 mol/L

For *pure* cmpds: $a_X = 1$

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An Example

Calculate ΔG for the following reaction:

$$CO\ (g) + 2H_2\ (g) \rightarrow CH_3OH\ (l)$$

Reaction Conditions:

T = 25. °C P_{CO} = 5.0 atm P_{H2} = 3.0 atm

First: **Find DG°**

$\Delta G^o_{rxn} = \Delta G^o_f\ (CH_3OH) - [\Delta G^o_f\ (CO) + 2\ \Delta G^o_f\ (H_2)]$

ΔG^o_{rxn} = (-166.35 kJ) - [(-137.15 kJ) + 2(0)]

ΔG^o_{rxn} = ***-29.20 kJ*** (= -2.920×10^4 J)

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On to ΔG!

Next: Find Q

$$Q = \frac{a_{CH3OH}}{(a_{CO})\,(a_{H2})^2} = \frac{1}{(5.0)\,(3.0)^2} = \mathbf{2.222 \times 10^{-2}}$$

Finally: Calculate ΔG

$\Delta G = \Delta G^o + RTLnQ$

$\Delta G = -2.920 \times 10^4 \text{ J} + (8.3145 \text{ J/mol-K})(298.15 \text{ K}) \text{ Ln}(2.222 \times 10^{-2})$

$\Delta G = -2.920 \times 10^4 \text{ J} + (-9.4366 \times 10^3 \text{ J})$

$\Delta G = -3.864 \times 10^4$ *J* = ***-39. kJ*** ← Spontaneous!

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How Does ΔG *Change* as the Reaction Proceeds?

Let's make it simple:

$A\ (g) \rightarrow B\ (g)$ $\quad \Delta G < 0$ (spontaneous)

So, we can write:

$G_A = G^o_A + RTLn(a_A)$

$G_B = G^o_B + RTLn(a_B)$

So, we start at:

$G_A > G_B$

As the reaction proceeds:

a_A *decreases* $\rightarrow G_A$ *DECREASES*

a_B **increases** $\rightarrow G_B$ **INCREASES**

DG ® 0

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Equilibrium

- Reaction will proceed until $\Delta G = 0$
- System is then at ***Equilibrium:***

$$A\ (g) \leftrightarrows B\ (g)$$

- Equilibrium is *dynamic:*
  - Rate of forward rxn = rate of reverse rxn
- Relationship with ΔG:

Equilibrium Constant

$$\Delta G = \Delta G^{o} + RT\,LnQ = 0$$

$$\mathbf{DG^{o} = -RTLnK}$$

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ΔG and K

$$\mathbf{DG^{o} = -RTLnK}$$

$\Delta G^{o} = 0$ then $K = 1$ (rxn at *equilibrium* when all in std states)

$\Delta G^{o} < 0$ then $K > 1$ (fwd rxn *spontaneous* from std states)

$\Delta G^{o} > 0$ then $K < 1$ (rev rxn *spontaneous* from std states)

K quantifies the relative balance between products and reactants *at equilibrium.*

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Calculating K from ΔG^o

Rearrange equation to solve for K:

$$LnK = \frac{\Delta G^o}{-RT}$$

For our CH_3OH formation example:

$$LnK = \frac{-2.92 \times 10^4 \text{ J}}{-(8.3145)(298.15K)} = 11.7791$$

only 1 sig fig!

$$K = e^{11.7791} = 1.30496 \times 10^5 = \mathbf{1. \times 10^5}$$

So: at equilibrium, *product* (CH_3OH) should predominate:

$K = 1. \times 10^5 = 1/[(a_{CO})(a_{H2})^2]$

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How about an example?

What is the vapor pressure of benzene at 25 ^oC, if **DG^o = 5.16 kJ/mol** for:

$$C_6H_6\ (l) \leftrightarrows C_6H_6\ (g)$$

What is K?

$K = a_{gas}/a_{liquid} = P_{gas}$ (vapor pressure of benzene!)

Knowing that: $\Delta G^o = -RTLnK$

$LnK = (5.16 \times 10^3 \text{ J/mol})/[(-8.3145 \text{ J/mol-K})(298.15 \text{ K})]$

$LnK = -2.08151 \Rightarrow K = 0.12474 = P_{gas}$

$P^o_{benzene} = 0.12474$ atm = ***95. torr***

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Effect of Temperature on K

- ΔG is temperature dependent, so:

At T_1: $\Delta G^o_1 = \Delta H^o - T_1\Delta S^o = -RT_1 LnK_1$

Solve for ΔS^o: $\Delta S^o = RLnK_1 + \Delta H^o/T_1$

At T_2: $\Delta S^o = RLnK_2 + \Delta H^o/T_2$

Combine, collect terms, rearrange:

$$\mathbf{Ln(K_2/K_1) = -(\Delta H^o/R)(1/T_2 - 1/T_1)}$$

Van't Hoff Equation

Endothermic: K *increases* with increasing temp

Exothermic: K **decreases** with increasing temp

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Clausius-Clapeyron *Revisited*

Recall, at any temperature T:

$$\Delta H^o - T\Delta S^o = -RTLnK$$

Now, solve for **LnK**:

$$\mathbf{LnK = (-\Delta H^o/R)(1/T) + \Delta S^o}$$

For the vaporization of a liquid:

A (l) ⇆ A (g) $K = a_{A(g)}/a_{A(l)} = P_A/1 = P_A$

Just substitute and, voila, we have C-C:

$$\mathbf{LnP_A = (-\Delta H^o_{vap}/R)(1/T) + \Delta S^o}$$

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Fun with Van't Hoff

- ➢ Use to measure ΔH^o
  - ✓ *Measure K* at different temperatures
  - ✓ *Plot* LnK versus 1/T
  - ✓ Straight line plot with ***slope*** **= $-\Delta H^o/R$**
- ➢ Can calculate ΔG^o from K
- ➢ Can calculate ΔS^o (from ΔH^o & ΔG^o)

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Big Example Problem

Let's look at this process to make ammonia:

$$\frac{1}{2}N_2\,(g) + 3/2\,H_2\,(g) \leftrightarrows NH_3\,(g)$$

Some thermodynamic constants:

ΔG^o_f:	0	0	-16.48 kJ/mol
ΔH^o_f:	0	0	-46.11 kJ/mol

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Spontaneous at 25 ^{o}C?

- Calculate ΔG^o_{rxn}:

$\Delta G^o = \Sigma\, \Delta G^o_f$ (products) - $\Sigma\, \Delta G^o_f$ (reactants)

$= \Delta G^o_f (NH_3) - [\frac{1}{2}\Delta G^o_f (N_2) + 3/2\Delta G^o_f (H_2)]$

= -16.48 kJ - 0

ΔG^o = ***-16.48 kJ*** Yes, reaction is spontaneous

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What is the value of K?

- From: $\Delta G^o = -RTLnK$

$$LnK = \frac{\Delta G^o}{-RT} = \frac{-16.48 \times 10^3 \text{ J}}{-(8.3145 \text{ J/mol-K})(298.15 \text{ K})} = 6.6479$$

Solving for K:

$K = e^{6.6479} = 7.7118 \times 10^2 = \mathbf{7.71 \times 10^2}$

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What is ΔS^o?

We need ΔH^o first:

$$\Delta H^o = \Sigma\ \Delta H^o_f\ \text{(products)} - \Sigma\ \Delta H^o_f\ \text{(reactants)}$$

$$= \Delta H^o_f\ (NH_3) - [\tfrac{1}{2}\Delta H^o_f\ (N_2) + 3/2\Delta H^o_f\ (H_2)]$$

$$= -46.11\ \text{kJ} - 0$$

ΔH^o = ***-46.11 kJ***

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Now, on to ΔS^o!

- Rearranging Gibbs-Helmholtz:

$$\Delta S^o = (\Delta H^o - \Delta G^o)/T$$

Substituting:

ΔS^o = [(-46,110 J - (-16,480 J))]/298.15 K

ΔS^o = -99.37951 J/K

ΔS^o = ***-99.38 J/K***

Why *negative?*

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At What Temperature Will NH_3 *Decompose*?

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

negative *negative*

- At a high enough temperature, ΔG^o will be *positive* and the reverse rxn will be spontaneous:

$T > \Delta H^o/\Delta S^o = -46{,}110 \text{ J}/-99.38 \text{ J/K}$

T > ***464.0 K***

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What is *K* at 1000 K?

Here's what we know:

$K_1 = 7.71 \times 10^2$ $K_2 = ?$

$T_1 = 298.15$ K $T_2 = 1000.$ K

Invoking van't Hoff:

$$\mathbf{Ln(K_2/K_1) = -(\Delta H^o/R)(1/T_2 - 1/T_1)}$$

$Ln(K_2/K_1) = -(-46{,}110 \text{ J}/8.3145 \text{ J/mol-K})[1/1000 - 1/298.15]$

$Ln(K_2/K_1) = (5.5457 \times 10^3)[-2.354 \times 10^{-3}] =$ ***-13.0547***

$K_2/K_1 = e^{-13.0547} = 2.1399 \times 10^{-6}$

$K_2 = (2.1399 \times 10^{-6})(7.71 \times 10^2) = 1.6502 \times 10^{-3} =$ ***1.7×10^{-3}***

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