

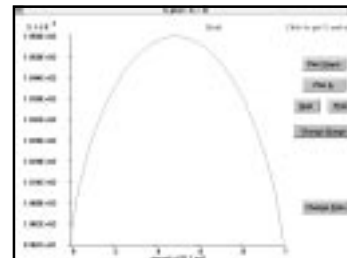
## Abstract

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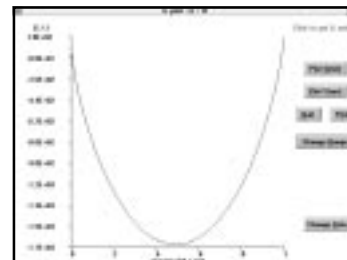
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G and S is designed to show Gibbs energy and entropy as a function of extent of reaction. It can be used to determine equilibrium compositions and changes in Gibbs energy and entropy for reactions, and to invite the exploration of differences and relationships between various thermodynamic properties. Changes in the system, surroundings, and universe are all available to show different ways in which the second law of thermodynamics can be used to determine the direction of spontaneous change and the position of equilibrium. It permits quantitative tests of qualitative predictions of the effect on equilibrium position following a change in the conditions.

G and S can be used as a lecture demonstration or as a dry lab for students to explore the interrelationship between Gibbs energy, entropy, and equilibrium. An extensive exercise illustrating many uses of the program is included.



Figures 1 and 2. Entropy and free energy plots from G and S.



This exercise uses G and S to illustrate the following:

1. Determination of equilibrium amounts by minimizing the Gibbs energy.
2. Equality of  $K_p$  obtained from these equilibrium amounts and from  $\Delta G^\circ = -RT \ln K_p$ .
3. Determination of equilibrium amounts by maximizing the entropy of the universe.
4. Demonstration that the maximum for  $S(\text{universe})$  occurs at a different position from the maximum for  $S(\text{system})$  emphasizing the primacy of  $S(\text{universe})$ .
5. Recognition of the relationship between the sign of  $\Delta H$  for the spontaneous process and the sign of  $\Delta S(\text{surroundings})$ .
6. Numerical confirmation of the results  $\Delta G = \Delta H(\text{sys}) - T\Delta S(\text{sys})$  and  $\Delta G = -T\Delta S(\text{universe})$ .
7. Confirmation (or otherwise) of qualitative predictions based on Le Châtelier's principle of the effect on the position of equilibrium of changing reaction conditions.
8. How to choose mole ratios of reactants so as to maximize yield of product or use of a particular reactant.

## Instructor Notes

The mathematics used in G and S assumes that the species being used are ideal gases, but within this limitation the formulation is exact. It is based on the fact that under conditions of constant temperature and pressure the direction of spontaneous change is such that the Gibbs energy decreases. At equilibrium the Gibbs energy is a minimum. It may be noted that the Gibbs energy of a substance can only be determined relative to some reference or standard state. What is tabulated is the Gibbs energy of formation. As we are only ever interested in changes in Gibbs energy, our inability to assign absolute values to  $G$  is no disadvantage.

G and S is intended for use by physical chemistry students. It could be used as a lecture-demonstration tool in class, or by students on their own.

## Answers to Questions in Student Assignment

Answers to the questions posed in the Student Assignment follow. Answers will vary as students may select any starting conditions within the bounds specified.

1. The volume is now  $2/3$  of the original volume. Explain why.

***P and T are constant so  $V \propto n$ . Because  $n$  decreases from 3 to 2,  $V$  decreases by a factor of  $2/3$ .***

2. Explain why the volume of C is now the same as the original volume of B, but the volume of A is half the original volume of A.

***P and T are constant so  $V \propto n$ .  
The amount of C equals the original amount of B, so volumes are equal. The amount of A equals half the original amount of A, so the volume is half.***

3. Explain why the partial pressures have the values given above.

***Because  $n$  and  $T$  are constant,  $PV$  is constant.  
The volume available to A is now  $3/2$  times as great, so  $P_A$  is  $2/3$  of its original value.  
The volume available to B is 3 times as great, so  $P_B$  is  $1/3$  of its original value.***

4. Explain why the partial pressure of A is now  $P_A^{i/2}$ .

*Let the original volume of B be  $V_B$  so that the original volume of A equals  $2V_B$  and the total original volume equals  $3V_B$ . The total volume in Figure 8c is  $2/3$  of the original total volume, i.e.  $2V_B$ . The amount of A has changed from 2 moles to 1 mole. So there is half the original amount of A in the same original volume therefore the partial pressure of A is half its original value.*

5. Show that the Gibbs energy change in  $c \rightarrow d$  in Figure 8 is  $2RT\ln 2$ .

$$\begin{aligned}\Delta G &= RT(\ln P_A^i + \ln(2P_C^i) - \ln(P_A^{i/2}) - \ln P_C^i) \\ &= RT(\ln(P_A^i/(P_A^{i/2})) + \ln(2P_C^i/P_C^i)) \\ &= RT(\ln 2 + \ln 2) \\ &= 2RT\ln 2\end{aligned}$$

6. Show that the Gibbs energy changes for the processes  $a \rightarrow b$  and  $c \rightarrow d$  are particular cases of the formula  $nRT\sum y_i \ln y_i$ .

$$\begin{aligned}a \rightarrow b: \Delta G &= nRT\sum y_i \ln y_i = 3RT((2/3)\ln(2/3) + (1/3)\ln(1/3)) \\ &= RT(2\ln(2/3) + \ln(1/3))\end{aligned}$$

$$\begin{aligned}d \rightarrow c: \Delta G &= nRT\sum y_i \ln y_i = 2RT((1/2)\ln(1/2) + (1/2)\ln(1/2)) \\ &= 2RT\ln(1/2)\end{aligned}$$

$$\text{so } c \rightarrow d \text{ has } \Delta G = -2RT\ln(1/2) = 2RT\ln 2$$

7. Use Eq. 8 and 9 to write expressions for  $K_p$  for each of the following:

|                                   | $K_p$ (Eq. 8)            | $K_p$ (Eq. 9)                    |
|-----------------------------------|--------------------------|----------------------------------|
| 1. $A \rightleftharpoons 2B$      | $(P_B^2/P_A)_{eq}$       | $(n_B^2/n_A)_{eq}(P/n)_{eq}$     |
| 2. $A + B \rightleftharpoons C$   | $(P_C/P_A P_B)_{eq}$     | $(n_C/n_A n_B)_{eq}(n/P)_{eq}$   |
| 3. $A + B \rightleftharpoons 2C$  | $(P_C^2/P_A P_B)_{eq}$   | $(n_C^2/n_A n_B)_{eq}$           |
| 4. $A + 2B \rightleftharpoons C$  | $(P_C/P_A P_B^2)_{eq}$   | $(n_C/n_A n_B^2)_{eq}(P/n)_{eq}$ |
| 5. $A + 2B \rightleftharpoons 3C$ | $(P_C^3/P_A P_B^2)_{eq}$ | $(n_C^3/n_A n_B^2)_{eq}$         |

8. For which of the above reactions is  $K_p$  independent of the applied pressure?

***All of them.  $K_p$  depends only on the temperature and is independent of the pressure.***

9. For which of the above reactions is the amount of each substance at equilibrium independent of the applied pressure?

***Those in which P does not appear in the Equation 9 expression for  $K_p$  i.e. reactions 3 and 5. There is no change in the total amount during these reactions.***

10. Write the reaction you chose and the expression for  $K_p$ .

***Chemical equation:  $A + 2B \rightleftharpoons C + D$***

***$K_p$  (Equation 9):  $(n_C n_D/n_A n_B^2)_{eq}(n/P)_{eq}$***

11. Record your values.

|  | A           | B           | C           | D           |
|--|-------------|-------------|-------------|-------------|
| $G / \text{J mol}^{-1}$                | <b>1000</b> | <b>3000</b> | <b>1500</b> | <b>3500</b> |
| $S / \text{J K}^{-1} \text{ mol}^{-1}$ | <b>10</b>   | <b>40</b>   | <b>30</b>   | <b>50</b>   |
| $n^i / \text{mol}$                     | <b>1</b>    | <b>1</b>    | <b>2</b>    | <b>2</b>    |
| $P / \text{atm}$                       | <b>1</b>    |             |             |             |
| $T / \text{K}$                         | <b>300</b>  |             |             |             |

12. Use Equations 3, 4 and 5 to check the calculation of  $\Delta G^\circ$ ,  $\Delta S^\circ(\text{sys})$  and  $\Delta H^\circ$ . Use  $\Delta G^\circ$  and Eq. 10 ( $R = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$ ) to calculate  $K_p$ . Use Eq. 1 and 2 ( $x = 0$ ) to check the calculation of  $G$  and  $S$  (initial).

$$\Delta G / \text{J mol}^{-1} = -2000$$

$$\Delta S / \text{J K}^{-1} \text{ mol}^{-1} = -10$$

$$\Delta H / \text{J mol}^{-1} = -5000$$

$$K_p = 2.2296$$

$$G(\text{initial}) / \text{J} = -5899.87$$

$$S(\text{initial}) / \text{J K}^{-1} = 276.33290$$

13. Use Equation 7 to calculate  $Q$  and predict whether the reaction goes forward or backward for your conditions.

$$Q = 24$$

***Predicted direction of spontaneous change: backward (to the left).***

14. Click on the bottom of the curve and record  $G$  and the amounts of all the species, shown at the top left of the screen when you click the mouse.

$$G(\text{equilibrium}) / \text{J} = -7341.58$$

|                              | A               | B               | C               | D               |
|------------------------------|-----------------|-----------------|-----------------|-----------------|
| $n^{\text{eq}} / \text{mol}$ | <b>1.523287</b> | <b>2.046574</b> | <b>1.476713</b> | <b>1.476713</b> |

$$n(\text{total}) / \text{mol} = 6.523287$$

15.  $K_p$  (Eq. 9) = **2.2296**

16. Comment on the agreement between the values of  $K_p$  calculated in boxes 12 and 15.

***They agree exactly.***

17. Record  $S(\text{total})$  and  $n_A$  at the maximum.

$$S(\text{total, equilibrium}) / \text{J K}^{-1} = \mathbf{281.13860}$$

$$n_A / \text{mol} = \mathbf{1.523287}$$

18. Is  $\Delta H$  for the *spontaneous* direction of reaction positive or negative?

***Positive***

Use  $\Delta H$  for the spontaneous direction of reaction to decide if heat flows to or from the surroundings and hence predict if  $S(\text{surroundings})$  should increase or decrease during the reaction.

***Heat flows from the surroundings.***

***$S(\text{surroundings})$  should decrease***

Does the slope of  $S(\text{surroundings})$  on the graph agree with your prediction?

***Yes***

19. Record  $S(\text{sys})$  and  $n_A$  at the maximum.

$$S(\text{sys}) / \text{J K}^{-1} = \mathbf{294.40007}$$

$$n_A / \text{mol} = \mathbf{2.069321}$$

20.  $S(\text{sys}) / \text{J K}^{-1}$  at  $n_{\text{A}}^{\text{eq}} = \mathbf{289.8600}$

21. Record the values of  $n_{\text{A}}$  at which a minimum appears for  $G$  and maxima for  $S(\text{total})$  and  $S(\text{system})$ . Comment on these values.

Value of  $n_{\text{A}}$  for minimum  $G$ :  $\mathbf{1.523287}$

Value of  $n_{\text{A}}$  for maximum  $S(\text{total})$ :  $\mathbf{1.523287}$

Value of  $n_{\text{A}}$  for maximum  $S(\text{system})$ :  $\mathbf{2.069321}$

***The minimum in  $G$  and the maximum in  $S(\text{total})$  lie at the same value of  $n_{\text{A}}$ . The maximum for  $S(\text{system})$  lies at a different value.***

22.  $G(\text{initial}) / \text{J} = \mathbf{-5889.87}$

$G(\text{equilibrium}) / \text{J} = \mathbf{-7341.58}$

$\Delta G / \text{J} = \mathbf{-1441.71}$

$S(\text{total, initial}) / \text{J K}^{-1} = \mathbf{276.33290}$

$S(\text{total, equilibrium}) / \text{J K}^{-1} = \mathbf{281.13860}$

$\Delta S(\text{total}) / \text{J K}^{-1} = \mathbf{4.80570}$

$-T\Delta S(\text{total}) / \text{J} = \mathbf{-1441.71}$

23.  $\Delta S(\text{sys}) / \text{J K}^{-1} = \mathbf{13.52710}$

$x / \text{mol} = \mathbf{-0.523287}$

$\Delta H(\text{sys}) / \text{J} = \mathbf{-2616.43}$

$\Delta H(\text{sys}) - T\Delta S(\text{sys}) / \text{J} = \mathbf{-1441.70}$

Compare  $\Delta G$  with both  $-T\Delta S(\text{total})$  and  $\Delta H(\text{sys}) - T\Delta S(\text{sys})$ .

***They are equal.***

24. Consider a mixture of  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  at equilibrium. Some  $\text{N}_2$  is added at fixed pressure (the volume increases to maintain constant pressure). Predict the effect on the amount of  $\text{NH}_3$  at the new equilibrium position.

*Answers will vary.*

|                          |  |                                    |                                    |
|--------------------------|--|------------------------------------|------------------------------------|
| 25.                      | $\text{N}_2$                           | $\text{H}_2$                       | $\text{NH}_3$                      |
| $n^i$ (first)            | 1                                      | 4                                  | 0                                  |
| $n^{\text{eq}}$ (first)  | <b>0.200746</b>                        | <b>1.602238</b>                    | <b>1.598508</b>                    |
| $n^i$ (second)           | $1 + n_{\text{A}}^{\text{eq}}$ (first) | $n_{\text{B}}^{\text{eq}}$ (first) | $n_{\text{C}}^{\text{eq}}$ (first) |
|                          | <b>1.200746</b>                        | <b>1.602238</b>                    | <b>1.598508</b>                    |
| $n^{\text{eq}}$ (second) | <b>1.056041</b>                        | <b>1.168124</b>                    | <b>1.887917</b>                    |

|                          |  |                                    |                                    |
|--------------------------|--|------------------------------------|------------------------------------|
| 26.                      | $\text{N}_2$                           | $\text{H}_2$                       | $\text{NH}_3$                      |
| $n^i$ (first)            | 1                                      | <b>0.25</b>                        | 0                                  |
| $n^{\text{eq}}$ (first)  | <b>09430508</b>                        | <b>0.0791524</b>                   | <b>0.1138984</b>                   |
| $n^i$ (second)           | $1 + n_{\text{A}}^{\text{eq}}$ (first) | $n_{\text{B}}^{\text{eq}}$ (first) | $n_{\text{C}}^{\text{eq}}$ (first) |
|                          | <b>1.9430508</b>                       | <b>0.0791524</b>                   | <b>0.1138984</b>                   |
| $n^{\text{eq}}$ (second) | <b>1.9468747</b>                       | <b>0.0906241</b>                   | <b>0.1062506</b>                   |

27. Compare the amounts of  $\text{NH}_3$  at equilibrium and comment on the direction of change in each of these cases:

1.  $n_{\text{B}}^i > 3n_{\text{A}}^i$

**More  $\text{NH}_3$  is produced. The reaction went to the right.**

2.  $n_{\text{B}}^i < n_{\text{A}}^i/3$

**Less  $\text{NH}_3$  is produced. The reaction went to the left.**

Do both results agree with your prediction?

*Answers will vary.*

28. Predict the effect on the equilibrium *concentration* of  $\text{NO}_2$  of decreasing the volume of an equilibrium mixture of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$ .

**Answers will vary.**

29.  $n(\text{N}_2\text{O}_4)$  initial / mol = **1.00000**  
 $n(\text{NO}_2)$  initial / mol = **1.00000**  
 Temperature / K = 298

|   |                 |                 |
|---|-----------------|-----------------|
| Pressure / atm  | <b>0.50000</b>  | <b>1.00000</b>  |
| $n(\text{N}_2\text{O}_4)$ final / mol   | <b>1.15296</b>  | <b>1.25125</b>  |
| $n(\text{NO}_2)$ final / mol  | <b>0.69407</b>  | <b>0.49748</b>  |
| $n(\text{total})$ / mol   | <b>1.84704</b>  | <b>1.74873</b>  |
| $K_p$ expression (Eq. 9): $(n(\text{NO}_2)^2/n(\text{N}_2\text{O}_4))_{eq} (P/n)$ |                 |                 |
| $K_p$ value   | <b>0.11311</b>  | <b>0.11311</b>  |
| Volume / L  | <b>90.332</b>   | <b>42.762</b>   |
| $[\text{N}_2\text{O}_4]$ / mol L <sup>-1</sup>                                    | <b>0.012764</b> | <b>0.029261</b> |
| $[\text{NO}_2]$ / mol L <sup>-1</sup>   | <b>0.007684</b> | <b>0.011634</b> |

30. State the effect of increasing the pressure on:

$n(\text{N}_2\text{O}_4)$  **increases**

$n(\text{NO}_2)$  **decreases**

$[\text{N}_2\text{O}_4]$  **increases**

$[\text{NO}_2]$  **increases**

Do the results agree with your prediction?

**Answers will vary.**

Comment on how meaningful is the expression “Reaction goes to the left” to describe the effect of increasing the pressure in this case.

**Applies to amounts but not to concentrations.**

31. Chemical equation:  $\text{A} + 2 \text{B} \rightleftharpoons \text{C}$

Value of a/b: **1/2**

Value of a/(b - c): **1**

|  |             |             |             |
|--|-------------|-------------|-------------|
| 32.  | A           | B           | C           |
| $G^\circ / \text{J mol}^{-1}$                | <b>1000</b> | <b>2000</b> | <b>3000</b> |
| $S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$ | <b>30</b>   | <b>20</b>   | <b>10</b>   |
| $P / \text{atm}$                             | <b>1</b>    |             |             |
| $T / \text{K}$                               | <b>298</b>  |             |             |

|           |               |                 |                   |                   |                   |                   |
|-----------|---------------|-----------------|-------------------|-------------------|-------------------|-------------------|
| 33.       | $n_A^i/n_B^i$ | $n_A^i/n_B^i$   | $n_A^{\text{eq}}$ | $n_B^{\text{eq}}$ | $n_C^{\text{eq}}$ | $y_C^{\text{eq}}$ |
| < a/b     | <b>0.2</b>    | <b>0.083005</b> | <b>0.766010</b>   | <b>0.116995</b>   | <b>0.121112</b>   |                   |
| = a/b     | <b>0.5</b>    | <b>0.299966</b> | <b>0.599932</b>   | <b>0.200034</b>   | <b>0.181860</b>   |                   |
| > a/b     | <b>0.8</b>    | <b>0.579810</b> | <b>0.559621</b>   | <b>0.220190</b>   | <b>0.161950</b>   |                   |
| < a/(b-c) | <b>0.8</b>    | <b>0.579810</b> | <b>0.559621</b>   | <b>0.220190</b>   | <b>0.161950</b>   |                   |
| = a/(b-c) | <b>1</b>      | <b>0.777709</b> | <b>0.555418</b>   | <b>0.222291</b>   | <b>0.142914</b>   |                   |
| > a/(b-c) | <b>2</b>      | <b>1.793279</b> | <b>0.586558</b>   | <b>0.206721</b>   | <b>0.079921</b>   |                   |

34. Write the value of  $n_A^i/n_B^i$  for which you find:

a. maximum mole fraction of C

**0.5**

b. maximum fractional conversion of B (minimum value of  $n_B^{\text{eq}}$ ).

**1**

Do these values agree with equations 11 and 12?

**Yes**