9.7: Exercises

1. For each of the following equations determine the optimum response using a one-factor-at-a-time searching algorithm. Begin the search at (0,0) by first changing factor *A*, using a step-size of 1 for both factors. The boundary conditions for each response surface are $0 \le A \le 10$ and $0 \le B \le 10$. Continue the search through as many cycles as necessary until you find the optimum response. Compare your optimum response for each equation to the true optimum. Note: These equations are from Deming, S. N.; Morgan, S. L. *Experimental Design: A Chemometric Approach*, Elsevier: Amsterdam, 1987, and pseudo-three dimensional plots of the response surfaces can be found in their Figures 11.4, 11.5 and 11.14.

(a) $R = 1.68 + 0.24A + 0.56B - 0.04A^2 - 0.04B^2$ $\mu_{opt} = (3,7)$

(b) $R = 4.0 - 0.4A + 0.08AB$ $\mu_{opt} = (10,10)$

(c) $R = 3.264 + 1.537A + 0.5664B - 0.1505A^2 - 0.02734B^2 - 0.05785AB$ $\mu_{opt} = (3.91,6.22)$

2. Use a fixed-sized simplex searching algorithm to find the optimum response for the equation in Problem 1c. For the first simplex, set one vertex at (0,0) with step sizes of one. Compare your optimum response to the true optimum.

3. A 2^k factorial design was used to determine the equation for the response surface in Problem 1b. The uncoded levels, coded levels, and the responses are shown in the following table. Determine the uncoded equation for the response surface.

A	*B*	*A**	*B**	response
8	8	+1	+1	5.92
8	2	+1	–1	2.08
2	8	–1	+1	4.48
2	2	–1	–1	3.52

4. Koscielniak and Parczewski investigated the influence of Al on the determination of Ca by atomic absorption spectrophotometry using the 2^k factorial design shown in the following table [data from Koscielniak, P.; Parczewski, A. *Anal. Chim. Acta* **1983**, *153*, 111–119].

$[Ca^{2+}]$ (ppm)	$[Al^{3+}]$ (ppm)	*Ca**	*Al**	response
10	160	+1	+1	54.92
10	0	+1	–1	98.44
4	16	–1	+1	19.18
4	0	–1	–1	38.52

(a) Determine the uncoded equation for the response surface.

(b) If you wish to analyze a sample that is 6.0 ppm Ca^{2+}, what is the maximum concentration of Al^{3+} that can be present if the error in the response must be less than 5.0%?

5. Strange [Strange, R. S. *J. Chem. Educ.* **1990**, *67*, 113–115] studied a chemical reaction using the following 2^3 factorial design.

factor	high (+1) level	low (–1) level
X: temperature	140°C	120°C
Y: catalyst	type B	type A
Z: [reactant]	0.50 M	0.25 M

run	*X**	*Y**	*Z**	% yield
1	–1	–1	–1	28

run	X^*	Y^*	Z^*	% yield
2	+1	–1	–1	17
3	–1	+1	–1	41
4	+1	+1	–1	34
5	–1	–1	+1	56
6	+1	–1	+1	51
7	–1	+1	+1	42
8	+1	+1	+1	36

(a) Determine the coded equation for this data.

(b) If β terms of less than ± 1 are insignificant, what main effects and what interaction terms in the coded equation are important? Write down this simpler form for the coded equation.

(c) Explain why the coded equation for this data can not be transformed into an uncoded form.

(d) Which is the better catalyst, A or B?

(e) What is the yield if the temperature is set to 125°C, the concentration of the reactant is 0.45 M, and we use the appropriate catalyst?

6. Pharmaceutical tablets coated with lactose often develop a brown discoloration. The primary factors that affect the discoloration are temperature, relative humidity, and the presence of a base acting as a catalyst. The following data have been reported for a 2^3 factorial design [Armstrong, N. A.; James, K. C. *Pharmaceutical Experimental Design and Interpretation*, Taylor and Francis: London, 1996 as cited in Gonzalez, A. G. *Anal. Chim. Acta* **1998**, *360*, 227–241].

factor	high (+1) level	low (–1) level
X: benzocaine	present	absent
Y: temperature	40°C	25°C
Z: relative humidity	75%	50%

run	X^*	Y^*	Z^*	color (arb. unit)
1	–1	–1	–1	1.55
2	+1	–1	–1	5.40
3	–1	+1	–1	3.50
4	+1	+1	–1	6.75
5	–1	–1	+1	2.45
6	+1	–1	+1	3.60
7	–1	+1	+1	3.05
8	+1	+1	+1	7.10

(a) Determine the coded equation for this data.

(b) If β terms of less than 0.5 are insignificant, what main effects and what interaction terms in the coded equation are important? Write down this simpler form for the coded equation.

7. The following data for a 2^3 factorial design were collected during a study of the effect of temperature, pressure, and residence time on the % yield of a reaction [Akhnazarova, S.; Kafarov, V. *Experimental Optimization in Chemistry and Chemical Engineering*, MIR Publishers: Moscow, 1982 as cited in Gonzalez, A. G. *Anal. Chim. Acta* **1998**, *360*, 227–241].

factor	high (+1) level	low (–1) level
X: temperature	200°C	100°C
Y: pressure	0.6 MPa	0.2 MPa
Z: residence time	20 min	10 min

run	*X**	*Y**	*Z**	% yield
1	–1	–1	–1	2
2	+1	–1	–1	6
3	–1	+1	–1	4
4	+1	+1	–1	8
5	–1	–1	+1	10
6	+1	–1	+1	18
7	–1	+1	+1	8
8	+1	+1	+1	12

(a) Determine the coded equation for this data.

(b) If β terms of less than 0.5 are insignificant, what main effects and what interaction terms in the coded equation are important? Write down this simpler form for the coded equation.

(c) Three runs at the center of the factorial design—a temperature of 150°C, a pressure of 0.4 MPa, and a residence time of 15 min —give percent yields of 8%, 9%, and 8.8%. Determine if a first-order empirical model is appropriate for this system at $\alpha = 0.05$.

8. Duarte and colleagues used a factorial design to optimize a flow-injection analysis method for determining penicillin [Duarte, M. M. M. B.; de O. Netro, G.; Kubota, L. T.; Filho, J. L. L.; Pimentel, M. F.; Lima, F.; Lins, V. *Anal. Chim. Acta* **1997**, *350*, 353–357]. Three factors were studied: reactor length, carrier flow rate, and sample volume, with the high and low values summarized in the following table.

factor	high (+1) level	low (–1) level
X: reactor length	1.3 cm	2.0 cm
Y: carrier flow rate	1.6 mL/min	2.2 mL/min
Z: sample volume	100 µL	150 µL

The authors determined the optimum response using two criteria: the greatest sensitivity, as determined by the change in potential for the potentiometric detector, and the largest sampling rate. The following table summarizes their optimization results.

run	*X**	*Y**	*Z**	ΔE (mV)	sample/h
1	–1	–1	–1	37.45	21.5
2	+1	–1	–1	31.70	26.0
3	–1	+1	–1	32.10	30.0
4	+1	+1	–1	27.30	33.0

5	–1	–1	+1	39.85	21.0
6	+1	–1	+1	32.85	19.5
7	–1	+1	+1	35.00	30.0
8	+1	+1	+1	32.15	34.0

(a) Determine the coded equation for the response surface where ΔE is the response.

(b) Determine the coded equation for the response surface where sample/h is the response.

(c) Based on the coded equations in (a) and in (b), do conditions that favor sensitivity also improve the sampling rate?

(d) What conditions would you choose if your goal is to optimize both sensitivity and sampling rate?

9. Here is a challenge! McMinn, Eatherton, and Hill investigated the effect of five factors for optimizing an H_2-atmosphere flame ionization detector using a 2^5 factorial design [McMinn, D. G.; Eatherton, R. L.; Hill, H. H. *Anal. Chem.* **1984**, *56*, 1293–1298]. The factors and their levels were

factor	high (+1) level	low (–1) level
A: H_2 flow rate	1460 mL/min	1382 mL/min
B: SiH_4	20.0 ppm	12.2 ppm
C: $O_2 + N_2$ flow rate	255 mL/min	210 mL/min
D: O_2/N_2 ratio	1.36	1.19
E: electrode height	75 (arb. unit)	55 (arb. unit)

The coded (“+” = +1, “–” = –1) factor levels and responses, *R*, for the 32 experiments are shown in the following table

run	*A**	*B**	*C**	*D**	*E**	*R*	run	*A**	*B**	*C**	*D**	*E**	*R*
1	–	–	–	–	–	0.36	17	–	–	–	–	+	0.39
2	+	–	–	–	–	0.51	18	+	–	–	–	+	0.45
3	–	+	–	–	–	0.15	19	–	+	–	–	+	0.32
4	+	+	–	–	–	0.39	20	+	+	–	–	+	0.25
5	–	–	+	–	–	0.79	21	–	–	+	–	+	0.18
6	+	–	+	–	–	0.83	22	+	–	+	–	+	0.29
7	–	+	+	–	–	0.74	23	–	+	+	–	+	0.07
8	+	+	+	–	–	0.69	24	+	+	+	–	+	0.19
9	–	–	–	+	–	0.60	25	–	–	–	+	+	0.53
10	+	–	–	+	–	0.82	26	+	–	–	+	+	0.60
11	–	+	–	+	–	0.42	27	–	+	–	+	+	0.36
12	+	+	–	+	–	0.59	28	+	+	–	+	+	0.43
13	–	–	+	+	–	0.96	29	–	–	+	+	+	0.23
14	+	–	+	+	–	0.87	30	+	–	+	+	+	0.51
15	–	+	+	+	–	0.76	31	–	+	+	+	+	0.13
16	+	+	+	+	–	0.74	32	+	+	+	+	+	0.43

(a) Determine the coded equation for this response surface, ignoring β terms less than ± 0.03.

(b) A simplex optimization of this system finds optimal values for the factors of *A* = 2278 mL/min, *B* = 9.90 ppm, *C* = 260.6 mL/min, and *D* = 1.71. The value of *E* was maintained at its high level. Are these values consistent with your analysis of the factorial design.

10. A good empirical model provides an accurate picture of the response surface over the range of factor levels within the experimental design. The same model, however, may yield an inaccurate prediction for the response at other factor levels. For this reason, an empirical model, is tested before it is extrapolated to conditions other than those used in determining the model. For example, Palasota and Deming studied the effect of the relative amounts of H_2SO_4 and H_2O_2 on the absorbance of solutions of vanadium using the following central composite design [data from Palasota, J. A.; Deming, S. N. *J. Chem. Educ.* **1992**, *62*, 560–563].

run	drops of 1% H_2SO_4	drops of 20% H_2O_2
1	15	22
2	10	20
3	20	20
4	8	15
5	15	15
6	15	15
7	15	15
8	15	15
9	22	15
10	10	10
11	20	10
12	15	8

The reaction of H_2SO_4 and H_2O_2 generates a red-brown solution whose absorbance is measured at a wavelength of 450 nm. A regression analysis on their data yields the following uncoded equation for the response (absorbance $\times$ 1000).

$$R = 835.90 - 36.82X_1 - 21.34X_2 + 0.52X_1^2 + 0.15X_2^2 + 0.98X_1X_2$$

where X_1 is the drops of H_2O_2, and X_2 is the drops of H_2SO_4. Calculate the predicted absorbances for 10 drops of H_2O_2 and 0 drops of H_2SO_4, 0 drops of H_2O_2 and 10 drops of H_2SO_4, and for 0 drops of each reagent. Are these results reasonable? Explain. What does your answer tell you about this empirical model?