

NELSON

SECOND CANADIAN EDITION

# CHEMISTRY

HUMAN ACTIVITY, CHEMICAL REACTIVITY

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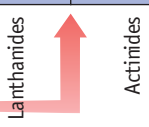
# Periodic Table of the Elements

1	Hydrogen 1 H											18 Helium 2 He						
2	Lithium 3 Li	Beryllium 4 Be											Fluorine 9 F	Neon 10 Ne				
3	Sodium 11 Na	Magnesium 12 Mg	Scandium 21 Sc	Titanium 22 Ti	Vanadium 23 V	Chromium 24 Cr	Manganese 25 Mn	Iron 26 Fe	Cobalt 27 Co	Nickel 28 Ni	Copper 29 Cu	Zinc 30 Zn	Aluminum 13 Al	Silicon 14 Si	Phosphorus 15 P	Sulfur 16 S	Chlorine 17 Cl	Argon 18 Ar
4	Potassium 19 K	Calcium 20 Ca	Scandium 21 Sc	Titanium 22 Ti	Vanadium 23 V	Chromium 24 Cr	Manganese 25 Mn	Iron 26 Fe	Cobalt 27 Co	Nickel 28 Ni	Copper 29 Cu	Zinc 30 Zn	Gallium 31 Ga	Germanium 32 Ge	Arsenic 33 As	Selenium 34 Se	Bromine 35 Br	Krypton 36 Kr
5	Rubidium 37 Rb	Strontium 38 Sr	Yttrium 39 Y	Zirconium 40 Zr	Niobium 41 Nb	Molybdenum 42 Mo	Technetium 43 Tc	Ruthenium 44 Ru	Rhodium 45 Rh	Palladium 46 Pd	Silver 47 Ag	Cadmium 48 Cd	Indium 49 In	Tin 50 Sn	Antimony 51 Sb	Tellurium 52 Te	Iodine 53 I	Xenon 54 Xe
6	Cesium 55 Cs	Barium 56 Ba	Lanthanum 57 La	Hafnium 72 Hf	Tantalum 73 Ta	Tungsten 74 W	Rhenium 75 Re	Osmium 76 Os	Iridium 77 Ir	Platinum 78 Pt	Gold 79 Au	Mercury 80 Hg	Thallium 81 Tl	Lead 82 Pb	Bismuth 83 Bi	Polonium 84 Po	Astatine 85 At	Radon 86 Rn
7	Francium 87 Fr	Radium 88 Ra	Actinium 89 Ac	Rutherfordium 104 Rf	Dubnium 105 Db	Seaborgium 106 Sg	Bohrium 107 Bh	Hassium 108 Hs	Meitnerium 109 Mt	Darmstadtium 110 Ds	Roentgenium 111 Rg	Copernicium 112 Cn	Ununtrium 113 Uut	Flerovium 114 Fl	Ununpentium 115 Uup	Livermorium 116 Lv	Ununseptium 117 Uus	Ununoctium 118 Uuo

  MAIN GROUP METALS  
  TRANSITION METALS  
  METALLOIDS  
  NON-METALS  
  PROPERTIES UNKNOWN

Uranium  
92  
U --- Atomic number  
U --- Symbol

Cerium 58 Ce	Praseodymium 59 Pr	Neodymium 60 Nd	Promethium 61	Samarium 62 Sm	Europium 63 Eu	Gadolinium 64 Gd	Terbium 65 Tb	Dysprosium 66 Dy	Holmium 67 Ho	Erbium 68 Er	Thulium 69 Tm	Ytterbium 70 Yb	Lutetium 71 Lu
Thorium 90 Th	Protactinium 91 Pa	Uranium 92 U	Neptunium 93 Np	Plutonium 94 Pu	Americium 95 Am	Curium 96 Cm	Berkelium 97 Bk	Californium 98 Cf	Einsteinium 99 Es	Fermium 100 Fm	Mendelevium 101 Md	Nobelium 102 No	Lawrencium 103 Lr



At the date of publication, elements 113, 115, 117 and 118 had not been named and have been given temporary names.

## STANDARD ATOMIC WEIGHTS OF THE ELEMENTS (IUPAC 2013)

Element	Symbol	Z	Standard Atomic Weight**	Working Values††	Element	Symbol	Z	Standard Atomic Weight**	Working Values††
Actinium*	Ac	89			Mendelevium*	Md	101		
Aluminum	Al	13	26.981 5385(7)	26.98	Mercury	Hg	80	200.592(3)	200.6
Americium*	Am	95			Molybdenum	Mo	42	95.95(1)	95.95
Antimony	Sb	51	121.760(1)	121.8	Neodymium	Nd	60	144.242(3)	144.2
Argon	Ar	18	39.948(1)	39.95	Neon	Ne	10	20.1797(6)	20.18
Arsenic	As	33	74.921 595(6)	74.92	Neptunium*	Np	93		
Astatine*	At	85			Nickel	Ni	28	58.6934(4)	58.69
Barium	Ba	56	137.327(7)	137.3	Niobium	Nb	41	92.906 37(2)	92.91
Berkelium*	Bk	97			Nitrogen	N	7	[14.006 43, 14.007 28]†	14.01
Beryllium	Be	4	9.012 1831(5)	9.012	Nobelium*	No	102		
Bismuth	Bi	83	208.980 40(1)	209.0	Osmium	Os	76	190.23(3)	190.2
Bohrium	Bh	107			Oxygen	O	8	[15.999 03, 15.999 77]†	16.00
Boron	B	5	[10.806, 10.821]†	10.81	Palladium	Pd	46	106.42(1)	106.4
Bromine	Br	35	[79.901, 79.907]†	79.90	Phosphorus	P	15	30.973 761 998(5)	30.97
Cadmium	Cd	48	112.414(4)	112.4	Platinum	Pt	78	195.084(9)	195.1
Calcium	Ca	20	40.078(4)	40.08	Plutonium*	Pu	94		
Californium*	Cf	98			Polonium*	Po	84		
Carbon	C	6	[12.0096, 12.0116]†	12.01	Potassium	K	19	39.0983(1)	39.10
Cerium	Ce	58	140.116(1)	140.1	Praseodymium	Pr	59	140.907 66(2)	140.9
Cesium	Cs	55	132.905 451 96(6)	132.9	Promethium*	Pm	61		
Chlorine	Cl	17	[35.446, 35.457]†	35.45	Protactinium*	Pa	91	231.035 88(2)	231.0
Chromium	Cr	24	51.9961(6)	52.00	Radium*	Ra	88		
Cobalt	Co	27	58.933 194(4)	58.93	Radon*	Rn	86		
Copernicium*	Cn	112			Rhenium	Re	75	186.207(1)	186.2
Copper	Cu	29	63.546(3)	63.55	Rhodium	Rh	45	102.905 50(2)	102.9
Curium*	Cm	96			Roentgenium*	Rg	111		
Darmstadtium*	Ds	110			Rubidium	Rb	37	85.4678(3)	85.47
Dubnium*	Db	105			Ruthenium	Ru	44	101.07(2)	101.1
Dysprosium	Dy	66	162.500(1)	162.5	Rutherfordium*	Rf	104		
Einsteinium*	Es	99			Samarium	Sm	62	150.36(2)	150.4
Erbium	Er	68	167.259(3)	167.3	Scandium	Sc	21	44.955 908(5)	44.96
Europium	Eu	63	151.964(1)	152.0	Seaborgium*	Sg	106		
Fermium*	Fm	100			Selenium	Se	34	78.971(8)	78.97
Flerovium*	Fl	114			Silicon	Si	14	[28.084, 28.086]†	28.09
Fluorine	F	9	18.998 403 163(6)	19.00	Silver	Ag	47	107.8682(2)	107.9
Francium*	Fr	87			Sodium	Na	11	22.989 769 28(2)	22.99
Gadolinium	Gd	64	157.25(3)	157.3	Strontium	Sr	38	87.62(1)	87.62
Gallium	Ga	31	69.723(1)	69.72	Sulfur	S	16	[32.059, 32.076]†	32.06
Germanium	Ge	32	72.630(8)	72.63	Tantalum	Ta	73	180.947 88(2)	180.9
Gold	Au	79	196.966 569(5)	197.0	Technetium*	Tc	43		
Hafnium	Hf	72	178.49(2)	178.5	Tellurium	Te	52	127.60(3)	127.6
Hassium*	Hs	108			Terbium	Tb	65	158.925 35(2)	158.9
Helium	He	2	4.002 602(2)	4.003	Thallium	Tl	81	[204.382, 204.385]†	204.4
Holmium	Ho	67	164.930 33(2)	164.9	Thorium*	Th	90	232.0377(4)	232.0
Hydrogen	H	1	[1.007 84, 1.008 11]†	1.008	Thulium	Tm	69	168.934 22(2)	168.9
Indium	In	49	114.818(1)	114.8	Tin	Sn	50	118.710(7)	118.7
Iodine	I	53	126.904 47(3)	126.9	Titanium	Ti	22	47.867(1)	47.87
Iridium	Ir	77	192.217(3)	192.2	Tungsten	W	74	183.84(1)	183.8
Iron	Fe	26	55.845(2)	55.85	Ununoctium*	Uuo	118		
Krypton	Kr	36	83.798(2)	83.80	Ununpentium*	Uup	115		
Lanthanum	La	57	138.905 47(7)	138.9	Ununseptium*	Uus	117		
Lawrencium*	Lr	103			Ununtrium*	Uut	113		
Lead	Pb	82	207.2(1)	207.2	Uranium*	U	92	238.028 91(3)	238.0
Lithium	Li	3	[6.938, 6.997]†	6.94	Vanadium	V	23	50.9415(1)	50.94
Livermorium*	Lv	116			Xenon	Xe	54	131.293(6)	131.3
Lutetium	Lu	71	174.9668(1)	175.0	Ytterbium	Yb	70	173.054(5)	173.1
Magnesium	Mg	12	[24.304, 24.307]†	24.31	Yttrium	Y	39	88.905 84(2)	88.91
Manganese	Mn	25	54.938 044(3)	54.94	Zinc	Zn	30	65.38(2)	65.38
Meitnerium*	Mt	109			Zirconium	Zr	40	91.224(2)	91.22

\*These elements have no stable isotopes and standard atomic weights are not listed, except for four of them (Bi, Th, Pa and U), which have characteristic terrestrial isotopic compositions with standard atomic weights given.

\*\*These are the current best estimates decided by IUPAC. The number in parentheses after each value indicates the uncertainty of estimation of the last digit.

†The variation in the atomic weights of these elements, depending on the origin and treatment of the sample, is greater than the uncertainty of their measurement. In these cases, the atomic weights are

listed by IUPAC as an interval; the two values listed are the upper and lower limits of the range of values.

††Where calculations of extremely high accuracy are not required, these working values (the standard atomic weights abridged to four significant figures) can be used. For those elements whose standard atomic weights are expressed as intervals, these are not abridged values, but working values selected by IUPAC from "conventional atomic weights." See Section 2.15.



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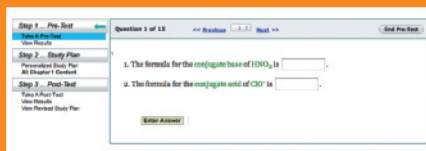
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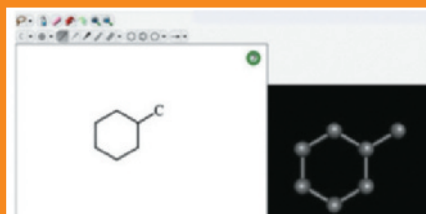
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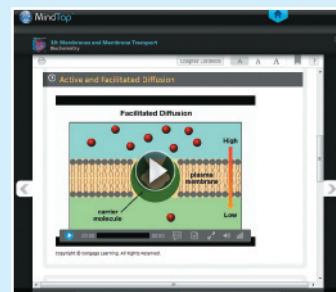
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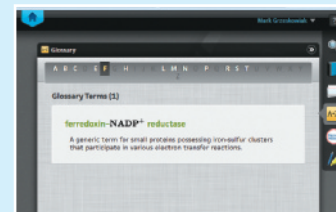
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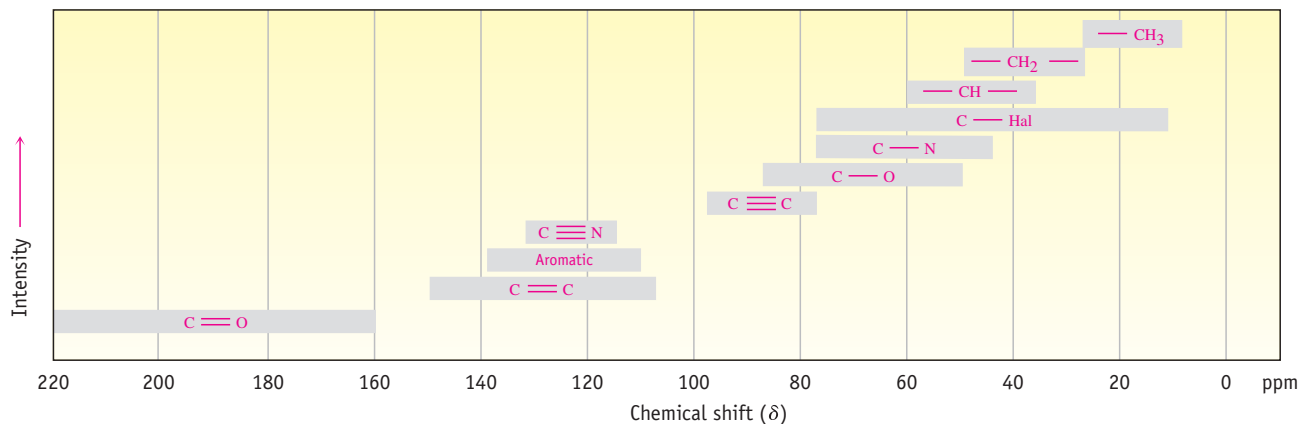
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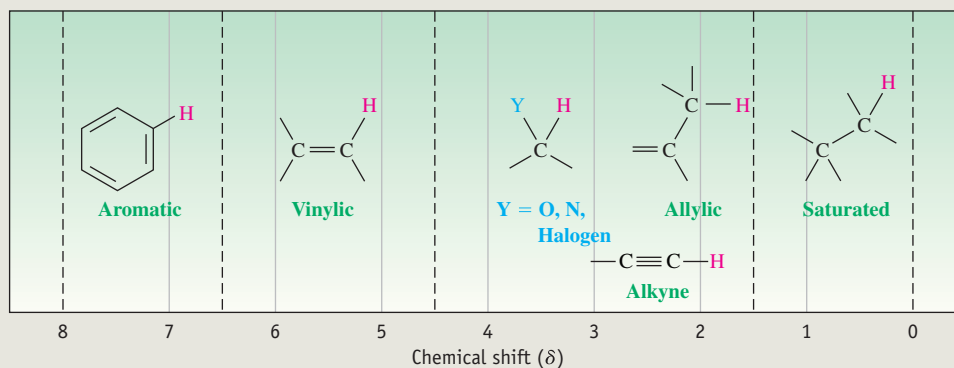
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## Correlation of $^{13}\text{C}$ Chemical Shift with Environment



## Correlation of $^1\text{H}$ Chemical Shift with Environment



Type of Hydrogen	Chemical Shift ( $\delta$ )	Type of Hydrogen	Chemical Shift ( $\delta$ )
Reference $(\text{CH}_3)_4\text{Si}$	0		
Saturated primary $-\text{CH}_3$	0.7–1.3	Alkyl halide $\text{X} = \text{Cl}, \text{Br}, \text{I}$	2.5–4.0
Saturated secondary $-\text{CH}_2-$	1.2–1.6	Alcohol	2.5–5.0 (Variable)
Saturated tertiary $\text{C}-\text{H}$	1.4–1.8	Alcohol, ether	3.3–4.5
Allylic $\text{C}=\text{C}-\text{C}-\text{H}$	1.6–2.2	Vinylic $\text{H}-\text{C}=\text{C}-\text{H}$	4.5–6.5
Methyl ketone $\text{C}(=\text{O})-\text{CH}_3$	2.0–2.4	Aromatic $\text{Ar}-\text{H}$	6.5–8.0
Aromatic methyl $\text{Ar}-\text{CH}_3$	2.4–2.7	Aldehyde $\text{C}(=\text{O})-\text{H}$	9.7–10.0
Alkynyl $-\text{C}\equiv\text{C}-\text{H}$	2.5–3.0	Carboxylic acid $\text{C}(=\text{O})-\text{O}-\text{H}$	11.0–12.0

## Common Functional Group Names and Their Characteristic IR Absorptions

Functional Group	Structure	Type of Absorption	Wavenumber (cm <sup>-1</sup> )	Intensity
<b>Hydrocarbons</b>				
alkane		C—H stretch	2850–2980	medium–strong
alkene		=C—H stretch	3020–3100	medium
		C=C stretch	1640–1670	weak–medium, sharp
aromatic ring		C—H stretch	3000–3100	medium
		ring vibrations	1585–1600, 1400–1500	strong, sharp
		out of plane C—H bending	675–900	strong
alkyne		≡C—H stretch	3270–3340	strong, sharp
		C≡C stretch	2100–2260	medium, sharp
<b>Carbonyl compounds</b>				
carbonyl group (general class of compounds)		C=O stretch (note 1)	1540–1870	strong, sharp
aldehyde		C=O stretch	1720–1740	strong
		C—H stretch (attached to C=O)	2700–2850	medium, 2 peaks
ketone		C=O stretch	1705–1725	strong
carboxylic acid		C=O stretch	1700–1725	strong
		O—H stretch	2500–3300	strong, very broad
ester		C=O stretch	1730–1750	strong
		C—O stretch	1000–1300	strong, 2 bands
amide		C=O stretch	1640–1700	strong
		N—H stretch	3400–3500	strong
		C—N—H bend	1590–1655	medium
acid chloride		C=O stretch	1785–1815	strong
<b>Other oxygen, nitrogen, and halogen compounds</b>				
alcohol		O—H stretch	3200–3550	strong, broad
		C—O stretch	1000–1260	strong, sharp
ether		C—O stretch	1085–1150	medium
amine		N—H stretch	3250–3400	medium
		C—N stretch	1020–1250	weak–medium
		C—N—H bend	1515–1650	medium–strong, sharp
nitrile		C≡N stretch	2210–2260	medium, very sharp
alkyl halide		C—F stretch (alkyl fluoride)	1000–1400	strong
		C—Cl stretch (alkyl chloride)	550–850	strong
		C—Br stretch (alkyl bromide)	515–690	strong
		C—I stretch (alkyl iodide)	500–600	strong
thiol		S—H stretch	2550–2600	weak
sulfide		C—S stretch	600–700	weak, variable
phosphate		P=O stretch	1250–1300	strong

Note 1: If the C=O group is conjugated with a C=C (i.e., C=C—C=O), the observed C=O absorption is shifted to lower wavenumbers by about 30 cm<sup>-1</sup>

SECOND CANADIAN EDITION

# CHEMISTRY

## HUMAN ACTIVITY, CHEMICAL REACTIVITY

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## Chemistry: Human Activity, Chemical Reactivity (CHACR): A Fully Integrated Print/Electronic Resource

### What Will the CHACR Student Experience?

The authors have designed and created *Chemistry: Human Activity, Chemical Reactivity* (CHACR) in ways consistent with their commitment to what should constitute a valuable learning experience in chemistry. A student who studies chemistry with CHACR will develop a sense of what modern chemistry is, why chemistry is important, what chemists do, how chemists have come to their current understandings, and what techniques chemists use to arrive at their shared understandings. The student will also appreciate the growth of chemical knowledge through interaction of observations, accepted “facts,” and modelling. These emphases, reflected in the title, are equally important for chemistry majors and for those who learn chemistry as a preparation for studies in other disciplines.

The CHACR student will arrive at this appreciation of chemistry as a human endeavour within the context of a body of knowledge that is clearly and rigorously presented, at an appropriate level for first-year university students. He or she will have benefitted from the authors’ knowledge of students’ learning of chemistry, derived from experience and participation in chemistry education research.

The CHACR student will experience chemistry from a number of perspectives that have governed CHACR’s design:

**1. The CHACR student will see chemistry as a human activity.** Chemistry is about more than chemicals and their structures. Chemistry is about people observing, experimenting, measuring, thinking, imagining, making sense, modelling, designing, communicating, and solving problems. The CHACR student will recognize that chemistry is done by people, and that it is possible for a student to be part of this chemistry community. This human activity pervades all of the discussion of chemical reactivity.



Courtesy of Professor Bob Hecht

Chemistry is presented as an engaging and worthwhile human activity.

**How?** The view of chemistry as an exciting human activity is emphasized by developing the chemistry content out of contemporary stories that illustrate how people come to understand and use chemical phenomena. In Chapter 1 and the opening section of all other chapters, students encounter “rich contexts” that emphasize the involvement of people in chemistry research and applications, and the ability of these people, through their accumulated knowledge, to solve problems and improve our quality of life. These rich contexts are designed to trigger in the CHACR student a motivation to understand the principles discussed within each chapter.

#### HUMAN ACTIVITY: BACTERIA WHISPERER

Bonnie Lynn Bassler (1962– )



Photo: Jeremy Dussan

*“Nature is trying to keep secrets from me, and my job is to find them out—to play the game against nature, and it’s fun and challenging.”*

For Princeton University scientist Bonnie Bassler, playing the game with nature has meant learning to listen to how micro-organisms communicate with each other. She has been called a “bacteria whisperer,” for her knack for learning the chemical language that bacteria speak. The idea that some of the simplest organisms on our planet not only communicate with each other through release of simple organic compounds, but make use of a common molecular language to speak with members of other species was revolutionary, and it launched Bassler to the forefront of her field.

*“My lab is a laughing, happy-go-lucky, loud, joke-playing place. But believe me, we do work. We are trying to understand how information gets in from the outside and how organisms manage multiple, simultaneous pieces of sensory information and correctly behave in response to these inputs. We’re never actually doing an experiment to answer those huge questions, but we are always picking at the edges of them. . . .”*

Ironically, Bassler started out her undergraduate education at the University of California, Davis, intending to become a veterinarian. But she feared “passing out” when it came to dissection, and she hated the memorization required in anatomy

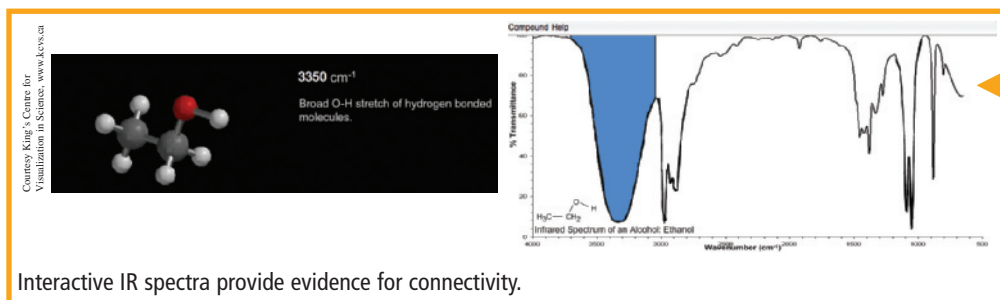
The sleuthing of chemists in Bonnie Bassler’s lab as they study how bacteria communicate with a chemical language is an exciting example of human activity in chemistry.

CHACR describes observable chemical behaviours *before* the ideas, theories, and models that are used to explain them: consistent with the nature of chemical progress, models are presented as human constructions to explain the facts, rather than as facts in themselves.

**2. The CHACR student will develop understandings of why chemists believe what they believe.** Chemistry students are usually expected to believe—solely on the authority of the instructor—a myriad of accepted “facts”: the composition of compounds, connectivity of atoms in molecules, bond angles, electronegativities of atoms in molecules, and molecular shapes, for example. The CHACR student gets some exposure to the methods that chemists use to obtain the evidence that gives them confidence in their “facts” and their models. What a pity it would be if chemistry students did not have a basic understanding of the sources of chemical knowledge. Could you imagine students in an astronomy course, for example, learning about our universe without some familiarity with how astronomers arrive at their knowledge?

**How?** The CHACR student is introduced relatively early, with the aid of interactive electronic resources, to various spectroscopic techniques for structure determination, at an understandable and usable level. One doesn't need to know the theory of IR or NMR spectroscopy or

mass spectrometry to use them for some purposes—any more than one needs to understand the thermodynamics of cars to use them. The relationships between structure and reactivity are emphasized: before presenting the structure of an ethanol molecule and the intermolecular forces between molecules, the student is asked to examine the physical properties



of the substance ethanol and the experimental spectroscopic evidence that leads to our models of the dependence of intermolecular forces on structure.

To take another example, in Chapter 8, the CHACR student is not simply presented with a mysterious notion of atomic orbitals, with meaningless quantum numbers plucked “out of the blue.” Rather, given periodic trends in atomic properties, CHACR raises the rigour bar to discuss how chemists came to rationalize the electronic structure in atoms, and quantum numbers are presented logically as particular values of parameters in the wave equation that give rise to standing waveforms. Again, one doesn't need to be able to solve the Schrödinger equation to obtain a sense of the origin of atomic quantum numbers.

**3. The CHACR student will see that chemistry is both contemporary and relevant.** The CHACR student will experience chemistry as a current, living, dynamic, and relevant subject, with the potential to improve the quality of life on our planet. He or she is exposed to samples of cutting-edge research and environmental and industrial applications integrated into the subject matter. In this way, the CHACR student will also develop a sense of the responsibility to use molecular sciences and technologies in sustainable and ethical ways.

**How?** The motivating contexts that open each chapter address topics such as drugs in sport, blood chemistry, methane clathrate hydrates, green chemistry, ocean acidification, bacterial communication, and alternative energy—all topical issues that exemplify the interaction of chemistry with our world and our lives, and that illustrate the importance of expanding our knowledge of chemistry.

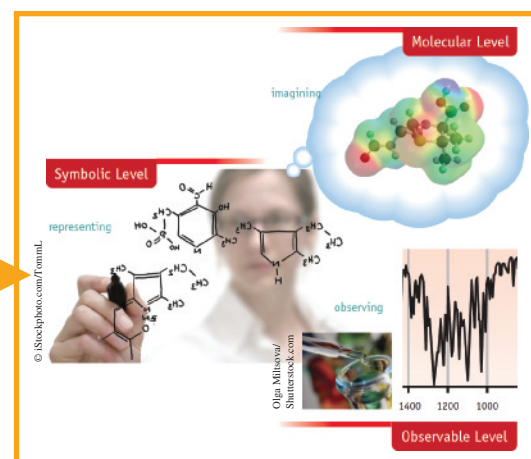
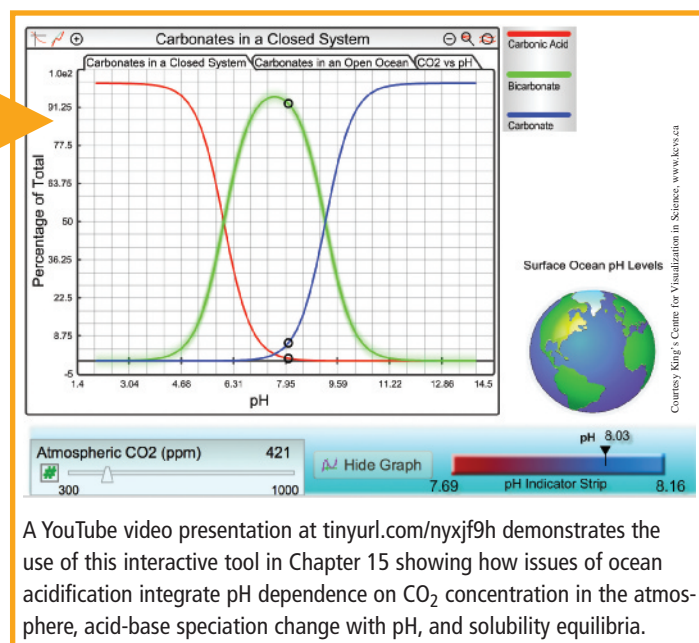
Particular emphasis is given to developing a basic understanding of the chemistry of our planetary life-support systems such as the atmosphere and oceans, and how they are dependent on human and natural activity.

For example, in the discussion of acid-base chemistry (Chapter 14), CHACR goes beyond the traditional treatment of percentage ionization of a solution of a weak acid (how often does one need to know the pH of a 0.01 mol L<sup>-1</sup> solution of propanoic acid?) to estimate the relative concentrations of protonated and deprotonated weak acid species when the pH of solution is governed by another agent. The calculations are simpler, but the significance much greater.

Cutting-edge chemistry from around the world is integrated into the coverage of chemistry concepts. Some Canadian examples include the following:

- David Dolphin and his research group in Vancouver have played a key role in the development of photodynamic therapy for the treatment of cancer and age-related macular degeneration.
- Virginia Walker at Queen's University studies antifreeze proteins in fish, which may be useful in preventing methane clathrate plugs in pipelines.
- The world-class Canadian Light Source in Saskatoon creates and stores a high-energy beam of electrons that produces synchrotron light that is one million times brighter than sunlight.
- Chemists at the National Research Council laboratories in Ottawa use solid-state nuclear magnetic resonance (NMR) spectroscopy to confirm the structures of new crystal polymorphs.
- Canada's Ballard Power is a world leader in hydrogen-oxygen fuel cell technology.
- Vaclav Smil in Manitoba has contributed to our understanding of the role of planetary nitrogen cycles, which has application both in the production of food and in our understanding of our atmosphere and oceans.

**4. The CHACR student is the beneficiary of findings from science education research.** There is, of course, more to teaching chemistry than presenting some words and symbols and hoping that students attain the same understanding as the teacher. The CHACR authors are familiar with a vast literature of research in chemistry education that has diagnosed inadequate understandings of even very able students, and that identifies characteristics of specific concepts and topics that present challenges to quality understanding.\* The authors have taken account of their



\* The following are a few of many such research papers:

Bent, H.A. (1984). "Uses (and Abuses) of Models in Teaching Chemistry." *Journal of Chemistry Education*, 61(9): 774.

Bucat, R. (2000). "Pedagogical Content Knowledge as a Way Forward." *Chemistry Education: Research and Practice*, 5(3): 215.

Coll, R.K., and Taylor, N. (2002). "Mental Models in Chemistry: Senior Chemistry Students' Mental Models of Chemical Bonding." *Chemistry Education: Research and Practice in Europe*, 3(2): 175.

Mahaffy, P. (2006). "Moving Chemistry Education into 3D: A Tetrahedral Metaphor for Understanding Chemistry." *Journal of Chemistry Education*, 83(1): 49.

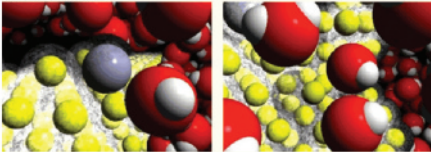
Tasker, R., & Dalton, R. (2006). "Research into Practice: Visualisation of the Molecular World Using Animations." *Chemistry Education Research and Practice*, 7(2): 141–59. See [tinyurl.com/k189xj7](http://tinyurl.com/k189xj7).



pedagogical content knowledge (knowledge about the teaching and learning of chemistry, over and above knowledge of chemistry itself) in the design and detail of CHACR.

→ **Molecular Modelling**  
e6.23 Watch an animation of hydrated silver ions reacting with copper atoms.

**What to do, and why.**  
Can you imagine what electron transfer from copper atoms to silver ions might be like at the molecular level? What is aquation, and why does it compete with electron transfer?



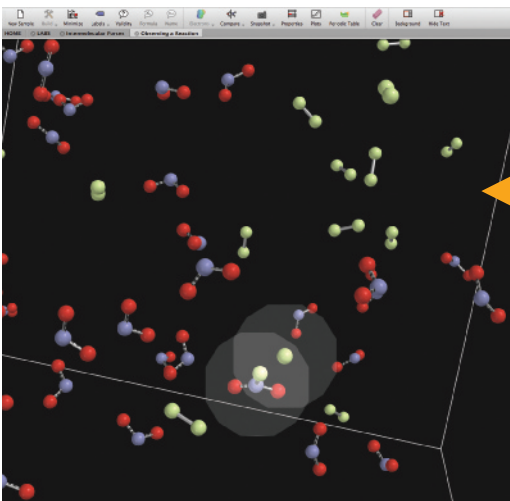
**Click here** to see an animation portraying electron transfer and aquation, and note how they are in competition with each other.

Courtesy of Dr. Roy Tasker

A YouTube video presentation at [tinyurl.com/k2x34sr](http://tinyurl.com/k2x34sr) demonstrates how the research-based *VisChem Learning Design* is used in CHACR to address specific misconceptions about reactions at the molecular level—in this case, the oxidation-reduction reaction between  $\text{Cu}(s)$  and  $\text{Ag}^+(aq)$ .

**(a) The triangle of chemistry operations.** The CHACR student develops an awareness of the three levels of operation in chemistry: (i) the observable level, pertaining to observable substances and phenomena; (ii) the molecular level of molecules, atoms, and ions, which is used to model chemical behaviour; and (iii) the symbolic level, involving language and symbolism that chemists use for communication and mathematical relationships. Lack of distinction among these is recognized as a major contributor to poor understanding of chemistry.

**How?** Four examples: First, the extraordinary electronic interactive resources that are a part of CHACR help the student to translate words, symbols, and equations into visualizations of the “reality.” Second, the CHACR student will recognize clearly, through many carefully worded examples, that chemists use models of the imagined world of atoms, molecules, and ions to explain observable chemical behaviour. Third, the CHACR student will distinguish among, for example, meanings of the symbol Na as the name of an element, a symbol for sodium atoms, and, as Na(s), a symbol for the substance sodium—thus avoiding potential confusion when this symbol is used in various contexts.



Two YouTube video presentations at [tinyurl.com/l2n5wr6](http://tinyurl.com/l2n5wr6) and [tinyurl.com/lgygnu9](http://tinyurl.com/lgygnu9) demonstrate our visualization approach using student-constructed simulations and prepared simulations in *Odyssey* to portray dynamic, many-particle mixtures and reactions.

CHACR does not say “the structure of sucrose” when we mean the structure of sucrose molecules, and neither does it talk about “axial and equatorial bonds in cyclohexane” (rather, “in cyclohexane molecules”). We believe that a few extra words can have a profound influence on students’ interpretations.

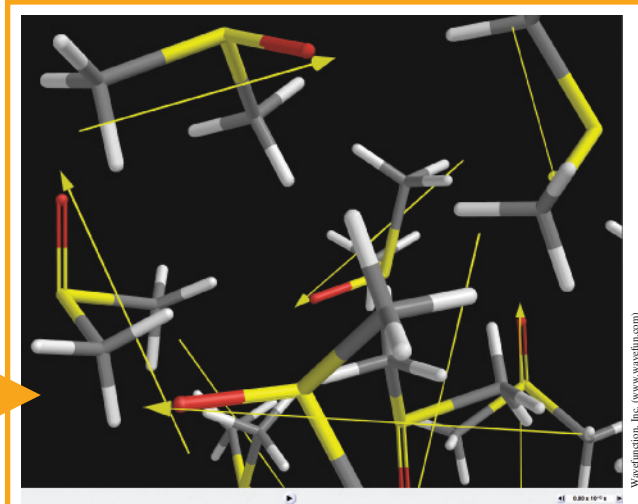
Fourth, reaction mechanisms are usually represented by structural equations that suggest the interaction of just one molecule or ion with another. Reaction kinetics only makes sense if we visualize a dynamic, many-particle reaction mixture in which events are controlled at least partly by probabilities. CHACR uses language that helps create such images, making it clear that the mechanistic equation refers to just one of billions of events that happen at various times.

**(b) A sequence of presentation based on the “need to know.”** The CHACR student will encounter some topics in two or more “bites” on a need-to-know basis—each time learning just enough chemistry to understand the current context. Although the topics are presented in the traditional sequence, this stepwise curriculum is designed to maintain the student’s interest.\* An understanding of any topic depends on understanding concepts, ideas, and relationships in others. The slightly interwoven presentation here contrasts with the usual single-block treatment of each topic that requires the student to trust in an eventual payoff in the future.

\* See, for example, Johnstone, A.H. (2000). “Teaching of Chemistry—Logical or Psychological?” *Chemistry Education: Research and Practice in Europe*, 1(1): 9–15.

**How?** For example, much of the chemistry presented beyond Chapter 7 depends on broad knowledge of the characteristics of precipitation reactions, oxidation-reduction reactions, acid-base reactions, and complexation reactions; these are described to sufficient levels in Chapter 6 long before these reaction types are discussed in more detail in Chapters 14–16. A basic idea of covalent bonding is presented in Chapter 3, while the theories of bonds are not discussed until Chapter 10. After all, one can do an awful lot of chemistry, recognizing that the molecules are held together by covalent bonds, without knowing about models of what a bond is.

In Chapter 6, the CHACR student can explore the dependence of molecular polarity on molecular shape. At that point, shapes of molecules are presented as “givens,” based on experimental evidence. The traditional use of the VSEPR model as a means of predicting shapes is not presented until Chapter 10. The authors believe that the consequences of molecular shape on intermolecular forces and properties should not be obfuscated by discussions of a model that attempts (with severe limitations) to rationalize those shapes.



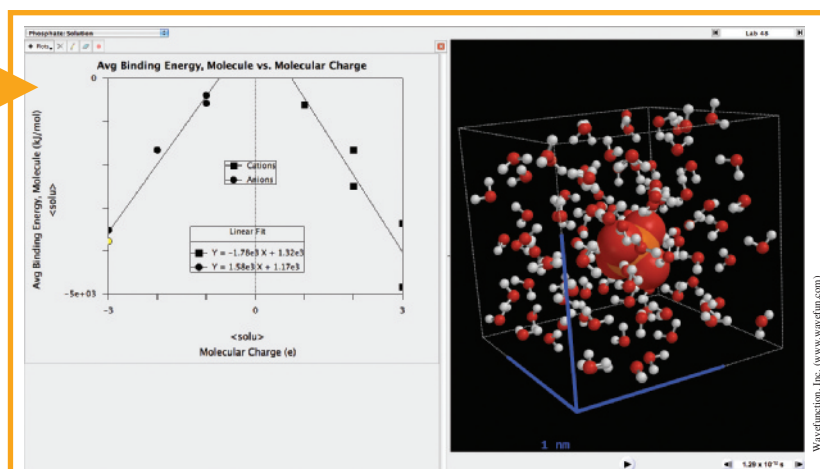
Frame from a dynamic simulation in *Odyssey* of dipole–dipole interactions between dimethylsulfoxide molecules in the liquid state. Dipoles are represented by yellow arrows.

**(c) Avoiding common student misconceptions.** The CHACR student will be less prone to common misconceptions that have been identified by research in students’ understandings of topics such as chemical equations, stoichiometry, and chemical equilibrium, for example.

**How?** By being aware of the findings of chemistry education research, the authors have been particularly clear in their approach, use of language, and explanations (including examples, analogies, and electronic resources) to lessen the likelihood of the misconceptions commonly identified. For example, the discussion entitled “What Chemical Equations Cannot Tell Us” explicitly lists common misconceptions of which students should be aware. The e-resources in CHACR are designed with the same pedagogical awareness in mind.

**5. The CHACR student will attain deep learning through visualizing the molecular world.** There is a valid argument that the ability to visualize molecules and ions, either singly or in aggregates such as reaction mixtures, is perhaps the single most important factor in achieving a deep understanding of chemistry. Static and dynamic visualizations bring meaning to the abstract notation of chemistry, and provide a molecular-level model for understanding macroscopic chemical behaviours. The CHACR student will develop particularly powerful explanatory powers through linking the macroscopic to the imagined submicroscopic world.

**How?** With a click, the CHACR student will be able to access molecular-level electronic resources that use computational molecular modelling to produce visual models (multi-particle simulations; electrostatic potential maps, bonding and polarity depictions) with real explanatory and predictive power to answer “What if . . . ?” questions. For example, the student will see simulations of the dissolution of sodium chloride in water, with focus on the process as a competition between opposing

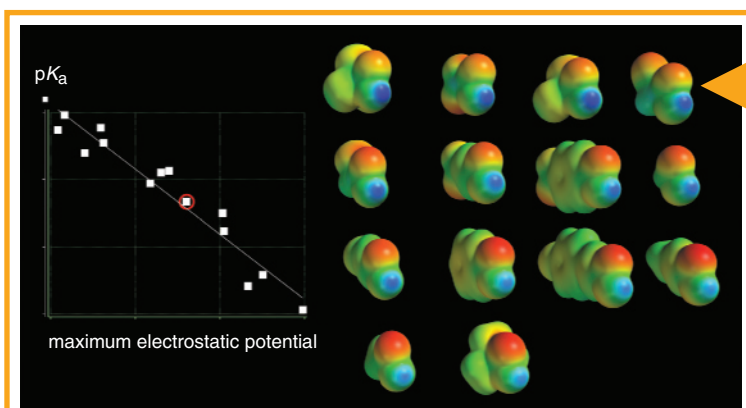


In *Odyssey*, students can plot data and discover relationships for themselves—in this case, between ionic charge and average binding energy due to aquation.



forces—crystal lattice forces opposed by aquation of the  $\text{Na}^+$  and  $\text{Cl}^-$  ions. He or she can see that the aquated ions are relatively independent, and that reactions are those of the individual aquated ions, rather than of a  $\text{NaCl}$  species.

The student can see simulations of melting of crystalline substances (such as ice), transient hydrogen bonding in substances and mixtures, and vibrational conformers of long-chain molecules. He or she can conduct *pseudo*-experiments on simulated gaseous systems, changing one of pressure, temperature, volume, or amount, and measuring and plotting the consequent change in another. A simulation of a chemical reaction (see point 4(a)) can demonstrate the decreasing concentration of reactant species, the increasing concentration of product species (giving meaning to the concept of reaction rate), and the approximately constant concentration of intermediates, as well as provide a basis for understanding why the rate of reaction might depend on reactant concentrations. The animations and simulations are informed by research showing common student misconceptions about chemical concepts.



The correlation of  $\text{pK}_a$  with maximum electrostatic potential on the carboxylic acid hydrogen in each of the models shown is rationalized in terms of the thermodynamics of aquation.

**6. The CHACR student will see less compartmentalization of organic and general chemistry.** The boundaries among organic chemistry, physical chemistry, inorganic chemistry, and biochemistry have merged at both the research and applied levels, and new interdisciplinary areas such as materials science, nanotechnology, and environmental science have taken on importance. The old compartmentalization will be much less visible to a CHACR student, and examples of new interfaces more visible.

**How?** CHACR encourages the student to link new ideas in one chemistry topic (e.g., acid-base chemistry) to another (e.g., organic mechanisms) without a distinction that they have moved to a different compartment. In the treatment of chemical kinetics, the CHACR student is exposed to examples taken from

inorganic chemistry as well as from organic chemistry (including nucleophilic substitution reactions). These are not seen as separate chemistries. To a large degree, there is a corresponding blended treatment of molecular stereochemistry with no suggestion that this is different for organic molecules than it is for inorganic molecules.

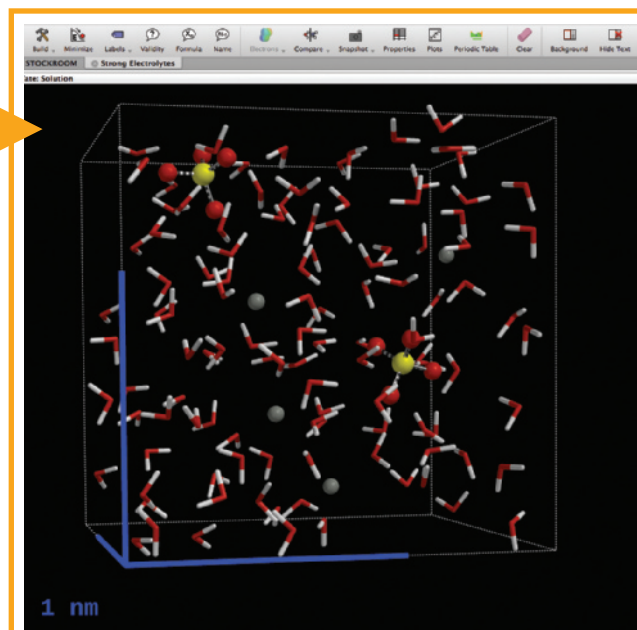
**7. The CHACR student will experience rigorous chemistry.** Rigour of treatment is not sacrificed to achieve the sorts of deep learning described previously through rich student-relevant contexts. On the contrary, rigour can assist deep learning—at least where *rigour* is taken to mean the validity and accuracy of the presentation of chemistry, rather than going to levels outside of the usefulness to first-year students. In this way, the CHACR student will have a sound preparation for future studies.

**How?** The answer to this question lies in a myriad of details and considerations to which the authors have attended. A few examples are presented here.

- Every type of reaction is presented as a competition process: precipitation as a competition between forces between ions in a crystal and aquation of the ions by polar water molecules; acid-base reactions as competition between species for  $\text{H}^+$  ions; oxidation-reduction reactions as competition for electrons; and complexation reactions as competition for Lewis bases.
- IUPAC conventions, units, and nomenclature are used consistently throughout this learning resource. The time is long gone when we should use local versions and expect the students to make conversions in the workplace.
- The significance of speciation is an important idea perpetuated through CHACR. So, for example, nowhere will the CHACR student encounter the symbolism “ $\text{Na}_2\text{SO}_4(\text{aq})$ ,”

which implies that there is an aquated species in solution with the formula  $\text{Na}_2\text{SO}_4$ . Instead, the CHACR student will visualize an aqueous sodium sulfate solution as one in which there are  $\text{Na}^+(\text{aq})$  and  $\text{SO}_4^{2-}(\text{aq})$  ions, in a 2:1 ratio and more or less independent of each other, with each type of ion contributing to the chemical behaviour of the solution.

- (d) It seems common elsewhere, in discussion of chemical equilibrium, to present a “magic” expression known as the equilibrium constant,  $K$ , and then to also introduce the reaction quotient,  $Q$ . The CHACR student is first introduced to the reaction quotient that can, in principle, have an infinite number of values, and which changes during the course of a reaction. The remarkable feature of  $Q$  is that it has the same value in all reaction mixtures in which a given reaction has reached the state of chemical equilibrium (at a given temperature): this numerical value is called the equilibrium constant at that temperature. This approach is consistent with the derivation of free energy changes and enthalpy changes in non-standard reaction mixtures from standard values.
- (e) The authors have been very careful to specify the conditions (constant temperature, pressure, etc.) under which relationships hold.
- (f) The language that chemists use among themselves is not necessarily appropriate for students. The authors have paid attention to re-packaging the language of advanced science communication into forms that are appropriate for first-year students, without losing validity.



Students can build their own simulation of, for example, sodium sulfate solution to see for themselves that there are no “aquated  $\text{Na}_2\text{SO}_4$  species in solution.”

## What’s New in the Second Edition?

***New Rich Contexts and Deeper Integration with Chemistry Concepts*** At the heart of the second edition of *Chemistry: Human Activity and Chemical Reactivity* (CHACR), are “rich contexts”—in Chapter 1 and introducing (through the first section) the chemistry content of each chapter. These stories describe current progress and issues in modern chemistry, give a sense of chemistry’s role in our world, and trigger motivation to learn more about the underlying principles. New rich context narratives, describing important ways in which chemistry takes on big challenges in our world and in the lives of ordinary people, have been written for this edition, including: “Artificial Leaves: Personal Energy Sources for Everyone by Mimicking Nature” (Chapter 16), “How Do Bacteria Tweet? Social Networking with Chemistry” (Chapter 21), and “The Serendipitous Discovery of Cisplatin, an Anti-Cancer Drug” (Chapter 23). Most of the other rich context narratives have been updated, and at the end of each chapter-opening section, connections of the narrative to chemistry principles in that and other chapters are explicitly listed, along with chapter references.

Feedback from instructors has indicated that use of the rich contexts is an important and distinguishing feature of CHACR, and that the narratives should be integrated even more deeply into the discussion of chemistry principles throughout the chapters. In the second edition, chapter discussions frequently refer to the issues raised in the trigger context stories. In some cases, the authors have added or enhanced a final chapter section that takes the chemistry principles discussed in the chapter full circle, back to more detailed discussions of the issues raised in the chapter-opening narrative. Examples include “Ocean Acidification Revisited Quantitatively” (Section 15.6), “Where There Is Methane, Is There Life?” (Section 4.7), and Bacterial Cross-Talk Revisited (Section 21.5).

***New Open-Ended Review Questions*** Students are helped to make connections between contexts that matter and chemistry principles through many new, open-ended

review questions that require additional research, reflection, and synthesis of ideas. These open-ended questions can be worked individually by students, and also lend themselves admirably to learning through peer-group discussions.

***Presentation of the Latest IUPAC Standards*** Since the first edition was published, the International Union of Pure and Applied Chemistry (IUPAC) has made significant changes in the values it assigns to the atomic weights of elements. These include the recognition that, for 12 elements, the variation of atomic weight (due to variation in isotopic distribution) from source to source is greater than the precision with which atomic weights can be measured. In these cases, the atomic weights are now listed as an interval, or span, of values. An understanding of this variability is crucial to chemists in forensic and other analyses, such as that described in the rich context story of Section 2.1: Falsely Positive? The Chemistry of Drugs in Sport. The second edition has added a new Section 2.13 to lead readers through the rationale for these changes and to give guidance on using the new values. CHACR lists the interval values of atomic weights of these 12 elements, as well as IUPAC-recommended working values called “conventional atomic weights,” needed, for example, when students carry out calculations involving unspecified samples. In addition, IUPAC determinations of recently updated values for the standard atomic weights of 19 other elements are listed.

***Organic Chemistry Coverage*** The philosophy of integrating examples from both inorganic and organic chemistry with fundamental principles from physical and analytical chemistry throughout the basic treatment of chemistry concepts is retained in the second edition. The organic chemistry needed for many first-year courses is adequately covered in Chapter 3 (*Models of Structure to Explain Properties*), Chapter 4 (*Carbon Compounds*), Chapter 9 (*Molecular Structures, Shapes, and Stereochemistry—Our Evidence*), and Chapter 10 (*Modelling Bonding in Molecules*). For courses offering a more detailed coverage of the chemistry of carbon compounds, we have responded to feedback from first edition users, and reduced the extent of organic chemistry from seven additional chapters to three (Chapters 19–21), some, or all of which, can be used to meet requirements. A new organizing idea to help students make sense of the myriad of reactions in organic chemistry, is to classify functional groups as *Levels 1–4*, based on the number of polar bonds between a carbon atom and electronegative heteroatoms such as O, N, S, Cl, and Br. Reviewers were enthusiastic about the potential that this classification scheme holds for organizing the content in these three chapters, and for helping students make sense of the challenging set of concepts related to oxidation and reduction reactions in organic chemistry. Those institutions requiring even more detailed coverage of organic chemistry can make use of the enhanced organic coverage in the second international edition, which retains seven full chapters on the chemistry of carbon compounds.

***Interactive Electronic Resources*** CHACR is a fully integrated print/electronic learning resource. We have received positive feedback on our extensive range of e-resources—interactive simulations, animations, tutorials, exercises, structure drawing tools, editable spreadsheets, and molecular-level building activities. This range continues to be unmatched by any chemistry textbook, providing students with various ways to engage with the rich contexts, obtain advice and feedback on calculations, visualize molecular structures and processes, and develop thinking skills using novel activities—all required for a deep understanding of chemistry.

The complete collection of e-resources is now more readily accessible from the dedicated *Interactive Tutorial and Visualisation Resources website* [www.nelson.com/chemistry2ce](http://www.nelson.com/chemistry2ce). Here, students and instructors can browse through the range of available e-resources, with or without reference to the margin icons in the textbook.

The molecular dynamics, force-field simulation software, *Odyssey*, is recommended to provide the immersive molecular-level visualization necessary to understand multi-particle phenomena (such as intermolecular forces and solvation, chemical speciation, reaction mechanisms); to interpret reactivity through electron distribution within molecules (using electrostatic potential maps); and to discover quantitative relationships by plotting changes

in properties in “molecular laboratories.” Many of the e-resources include structure and simulation files that need to be opened in *Odyssey*. Instructors are now able to design their own activities using this software, and assign them for marks.

Developments in the wide range of chemistry resources and visualization tools in the *King’s Centre for Visualization in Science* have led to more interactive learning experiences integrated with the rich context narratives and chemistry concepts in CHACR. The simulation tools have been improved, particularly those demonstrating the power of IR and NMR spectroscopy and mass spectrometry to reveal molecular structure. The information on climate change chemistry has been updated, with new resources to address “What if . . . ?” questions. There are now more case studies involving applications of the state-of-the-art technique of isotope ratio mass spectrometry to show students how chemists work to solve challenging and significant problems.

**Glossary and Index** The authors have received considerable feedback that indicates that students find the glossary of terms very useful. Consistent with this feedback, we have included many more terms. Students who use the e-book will find it particularly useful that a pop-up explanation of terms appearing in bold font will appear when the cursor hovers over the term.

No text is perfect. Although the readability and clarity of ideas in the first edition has been highly praised, the authors have considered line by line how to improve the expression of ideas, as well as how to attend to pedagogical improvements.

## Visual Tour of E-learning Resources

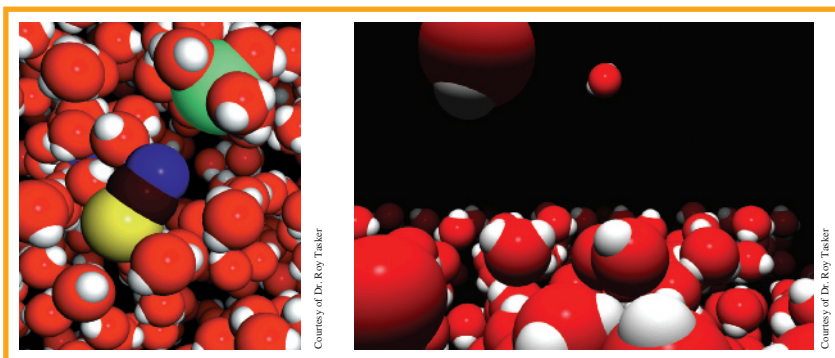
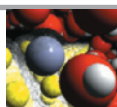
In the margins of each chapter, distinct icons point to e-resources that offer a rich variety of electronic experiences students can access for learning either on their own or with other students. Access the complete collection of e-resources at [www.nelson.com/chemistry2ce](http://www.nelson.com/chemistry2ce).

### Molecular Modelling

Students will be immersed in the molecular world through models and animations. Using their rich mental models, students are able to visualize and thereby interpret the subtlety and meaning of symbolic formulas, equations for reactions, and the mathematical relationships between quantities.

#### Molecular Modelling

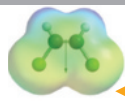
e2.1 Represent molecular structures using models and structural formulas.





### Molecular Modelling (Odyssey)

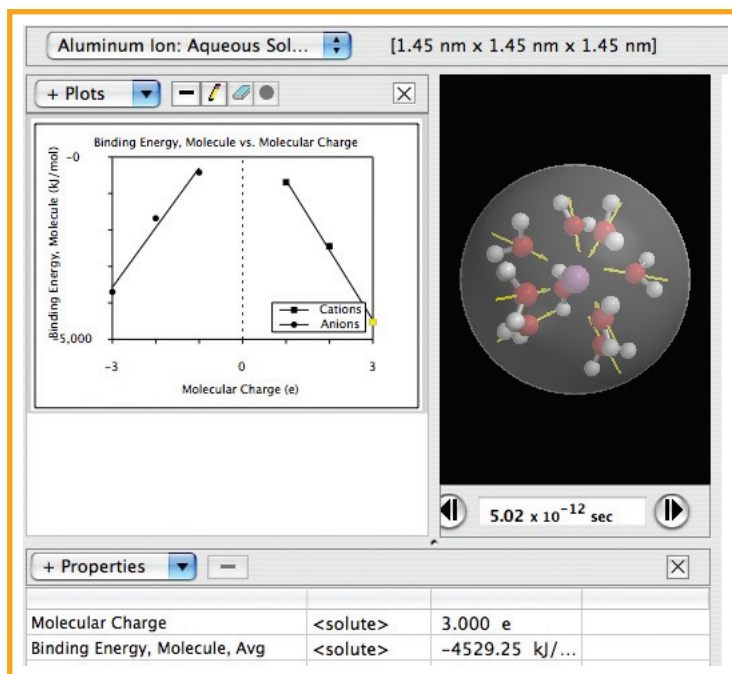
e2.4 Compare simulations of solid, liquid, and gaseous bromine.



### Molecular Modelling (Odyssey)

Through building molecular models and constructing solution simulations of ions and molecules in *Odyssey*, students will acquire, at the molecular level, a “feel” for molecular flexibility and freedom of movement. Students can measure bond distances and approximate energies, change the temperature and pressure, and plot the results to discover mathematical relationships. In this way, students are able to experiment in a “molecular sandbox”!

temperature and pressure, and plot the results to discover mathematical relationships. In this way, students are able to experiment in a “molecular sandbox”!



### Think about It

These interactive resources involve active problem solving with immediate feedback. Some require interpretation of laboratory videos; others, manipulation of simulations.

### Think about It

e2.3 See how IRMS can detect cheating.

#### Exploring Chemical Reactions 1

Question 4 of 9

Which of the following might be responsible for the delay in the start of the reaction?

- The Al needs to first dissolve in the liquid Br<sub>2</sub>.
- The Al first needs to vaporize into a gas, which is seen as smoke coming out of the beaker.
- The Al has a thin coating of aluminum oxide, and it takes some time for the Br<sub>2</sub> to penetrate this coating.
- The Al must first react with all of the O<sub>2</sub> dissolved in the Br<sub>2</sub> before it will react with the Br<sub>2</sub>.

Solve It

Photo: Charles D. Winters

Interpreting observations

Chemical shift = 29.78 ppm. Alkane carbon.

Spectroscopic evidence for non-equivalence

## Background Concepts and Taking It Further

These resources are intended for students who need to review prerequisite knowledge and skills and those wishing more detail on a topic. They are listed in the Chapter Outline on the first page of each chapter.

### Background Concepts

**e2.16** Read about Amedeo Avogadro and the constant named in his honour.



### Taking It Further

**e12.10** Read about how solutes raise the boiling point of a solution.



Photo: Charles D. Winters



Unbalanced Reaction Equation:  
 $\text{Fe}^{2+}(\text{aq}) + \text{MnO}_4^{-}(\text{aq}) \longrightarrow \text{Fe}^{3+}(\text{aq}) + \text{Mn}^{2+}(\text{aq})$

▶ || ◀ ◀ ▶▶

Questions

Question 3/4

How many electrons does  $\text{MnO}_4^{-}$  gain during the reaction?

Submit

Back
Next

Intro Questions

## Web Link

This resource provides students with links to sites that illustrate the application of chemistry to real problems and the latest developments in research, such as the Protein Data Bank database of molecular structures.

### Web Link

**e2.2** Why is the issue of ethics in chemistry so important?



Help

How can 400,000 years of temperature data be determined from ice core samples?

How is synthetic testosterone detected in professional athletes?

All of these examples rely on a technique called Isotope Ratio Mass Spectrometry (IRMS).  
Click on one to learn more!

How can you tell if your honey has been diluted with sugar syrup?

How do scientists discover the sources of methane molecules on Earth and on Mars?

Source: King's Centre for Visualization in Science, www.kovs.ca



### Interactive Exercises 2.18–2.20

Practise converting between masses and numbers of particles.



### Interactive Exercises

Students can complete these exercises and receive immediate feedback. For the more challenging problems, students can access stepwise tutorial assistance for suggested strategies for solving the problems.

MAIN QUESTION	<p><b>Question</b></p> <p>You have 0.288 g of an unknown acid, H<sub>2</sub>A, which reacts with NaOH according to the balanced equation</p> $\text{H}_2\text{A}(\text{aq}) + 2 \text{NaOH}(\text{aq}) \longrightarrow \text{Na}_2\text{A}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$ <p>If 36.04 mL of 0.239 M NaOH is required to titrate the acid to the equivalence point, what is the molar mass of the acid?</p>	<p><b>Answer</b></p> <p>Enter a response, then Submit.</p> <p><input type="text" value="33.52"/> g/mol</p> <p><input type="button" value="Submit"/></p> <p><b>INCORRECT.</b> Answer tutorial questions.</p>
	<p><b>Step 1 of 4</b></p> <p>What volume of NaOH solution, in liters, is used in the titration?</p>	<p><b>Answer</b></p> <p>Enter a response, then Submit.</p> <p><input type="text"/> L</p> <p><input type="button" value="Submit"/></p>
TUTORIAL QUESTION		

The second edition of *Chemistry: Human Activity, Chemical Reactivity* uses the best of print and digital resources to bring chemistry into the 21st century. Visualization and interactivity are elevated to a new level by integrating text features that connect the print content to digital assets, such as the MindTap Reader, *Odyssey*, Online Web Learning (OWL), Organic Chemistry Flashware, and more.

## OWLv2<sup>®</sup>



Developed by teaching chemists, OWL is the leading online learning system for chemistry. Conceived over a decade ago at the University of Massachusetts, OWL is now the world's most widely used online chemistry solution, trusted by hundreds of thousands of learners to improve their chemistry performance and grades.

OWL from Cengage Learning uses a mastery learning approach, meaning students continue working problems until they show they have mastered the concept. Each time a student tries a problem, OWL changes the chemicals, numbers, and wording of the question to assess and ensure understanding of the underlying concept. OWL gives students resources to practise chemistry at their own pace, visualize chemical concepts, improve their problem-solving skills, and earn better grades. Users can find a wealth of varied content—including tutorials, interactive simulations, visualization exercises, active figures, drawing tools, and more—to address different learning styles.

OWLv2 delivers all the depth, power, and reliability that have made this resource the most trusted chemistry learning system for more than a decade. And now it adds remarkable new instructor and learner enhancements to better help students master the subject.

New functionality in OWLv2:

- The “Are You Sure” window alerts students to errors prior to answer submission
- OWLv2 allows students to draw chemical structures directly in their assignment using ChemDoodle Sketcher
- New, more intuitive assignment settings and options give you increased control
- Fully integrated gradebook—no set up required
- And much more!

## About the Nelson Education Teaching Advantage (NETA)

The **Nelson Education Teaching Advantage (NETA)** program delivers research-based instructor resources that promote student engagement and higher-order thinking to enable the success of Canadian students and educators. To ensure the high quality of these materials, all Nelson ancillaries have been professionally copy-edited.

Be sure to visit Nelson Education's **Inspired Instruction** website at <http://www.nelson.com/inspired> to find out more about NETA. Don't miss the testimonials of instructors who have used NETA supplements and seen student engagement increase!



**Planning Your Course** *NETA Engagement* presents materials that help instructors deliver engaging content and activities to their classes. **NETA Instructor's Manuals** not only identify the topics that cause students the most difficulty, but also describe techniques and resources to help students master these concepts. Dr. Roger Fisher's *Instructor's Guide to Classroom Engagement* accompanies every Instructor's Manual.

**Assessing Your Students** *NETA Assessment* relates to testing materials. **NETA Test Bank** authors create multiple-choice questions that reflect research-based best practices for constructing effective questions and testing not just recall but also higher-order thinking. Our guidelines were developed by David DiBattista, psychology professor at Brock University and 3M National Teaching Fellow, whose research has focused on multiple-choice testing. All Test Bank authors receive training at workshops conducted by Prof. DiBattista, as do the copy-editors assigned to each Test Bank. A copy of *Multiple Choice Tests: Getting Beyond Remembering*, Prof. DiBattista's guide to writing effective tests, is included with every Nelson Test Bank.

**Teaching Your Students** *NETA Presentation* has been developed to help instructors make the best use of Microsoft® PowerPoint® in their classrooms. With a clean and uncluttered design developed by Maureen Stone of StoneSoup Consulting, **NETA PowerPoints** features slides with improved readability, more multi-media and graphic materials, activities to use in class, and tips for instructors on the Notes page. A copy of *NETA Guidelines for Classroom Presentations* by Maureen Stone is included with each set of PowerPoint slides.

**Technology in Teaching** *NETA Digital* is a framework based on Arthur Chickering and Zelda Gamson's seminal work "Seven Principles of Good Practice In Undergraduate Education" (AAHE Bulletin, 1987) and the follow-up work by Chickering and Stephen C. Ehrmann, "Implementing the Seven Principles: Technology as Lever" (AAHE Bulletin, 1996). This aspect of the NETA program guides the writing and development of our **digital products** to ensure that they appropriately reflect the core goals of contact, collaboration, multimodal learning, time on task, prompt feedback, active learning, and high expectations. The resulting focus on pedagogical utility, rather than technological wizardry, ensures that all of our technology supports better outcomes for students.

## Instructor Resources

All NETA and other key instructor ancillaries are provided on the Instructor Companion Site at [www.nelson.com/chemistry2ce](http://www.nelson.com/chemistry2ce), giving instructors the ultimate tool for customizing lectures and presentations. The NETA PowerPoint slides, Image Library, and Turning Point slides are also available on the **Instructor's Resource CD** (ISBN 0-17-656870-0).

## NETA Test Bank

This resource was written by Brett McCollum, Mount Royal University. It includes over 1000 multiple-choice questions written according to NETA guidelines for effective construction and development of higher-order questions. The Test Bank was copy-edited by a NETA-trained



editor and reviewed by David DiBattista for adherence to NETA best practices. Also included are true/false, completion, short answer, matching, problem, and essay type questions.

The NETA Test Bank is available in a new, cloud-based platform. **Testing Powered by Cognero®** is a secure online testing system that allows you to author, edit, and manage test bank content from any place you have Internet access. No special installations or downloads are needed, and the desktop-inspired interface, with its drop-down menus and familiar, intuitive tools, allows you to create and manage tests with ease. You can create multiple test versions in an instant, and import or export content into other systems. Tests can be delivered from your learning management system, your classroom, or wherever you want.

### NETA PowerPoint

Microsoft® PowerPoint® lecture slides for every chapter have been created by Philip Elder. These slides feature key figures, tables, and photographs from the second edition of *Chemistry: Human Activity, Chemical Reactivity*. NETA principles of clear design and engaging content have been incorporated throughout, making it simple for instructors to customize the deck for their courses.

### Image Library

This resource consists of digital copies of figures, short tables, and photographs used in the book. Instructors may use these jpegs to customize the NETA PowerPoint or create their own PowerPoint presentations.

### NETA Instructor's Manual

This resource was written by Rabin Bissessur, University of Prince Edward Island. It is organized according to the textbook chapters and addresses key educational concerns, such as typical stumbling blocks student face and how to address them.

### Instructor's Solutions Manual

This manual, prepared by Jillian Hatnean, University of Toronto, and Mark Vaughan, Capilano University, has been independently checked for accuracy by Rabin Bissessur, University of Prince Edward Island. It contains complete solutions to all exercises in the book.

### DayOne

**DayOne—Prof InClass** is a PowerPoint presentation that instructors can customize to orient students to the class and their text at the beginning of the course.

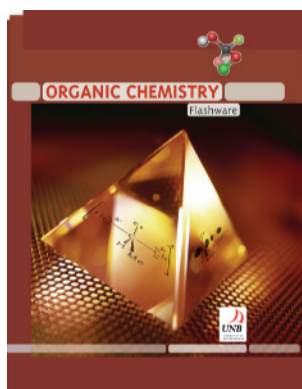
### TurningPoint®

Another valuable resource for instructors is **TurningPoint® classroom response software** customized for the second edition of *Chemistry: Human Activity, Chemical Reactivity*. This resource was written by Jeff Landry, McMaster University. Now you can author, deliver, show, access, and grade, all in PowerPoint, with no toggling back and forth between screens. With JoinIn you are no longer tied to your computer. You can walk about your classroom as you lecture, showing slides and collecting and displaying responses with ease. If you can use PowerPoint, you can use JoinIn on TurningPoint. (Contact your Nelson publishing representative for details.)

### Organic Chemistry Flashware

<http://flashchem.nelson.com>

**Organic Chemistry Flashware** is a collection of interactive web-based courseware designed to give step-by-step control over reaction mechanisms, with simultaneous multiple representations of orbitals, energy changes, and electron movements. This collection of over 130 learning objects has been produced to enhance the traditional lecture experience and is optimized for both the individual computer user and classroom projection.



## Student Learning Resources

The second edition of *Chemistry: Human Activity, Chemical Reactivity with OWLv2* will help you succeed in chemistry through its integrated, step-by-step approach to problem solving and its easy-to-understand presentation.

### OWLv2

Developed by teaching chemists, **OWL** is the leading online learning system for chemistry. Conceived over a decade ago at the University of Massachusetts, OWL is now the world's most widely used online chemistry solution, trusted by hundreds of thousands of learners to improve their chemistry performance and grades.

OWLv2 gives students resources to practise chemistry at their own pace, visualize chemical concepts, improve their problem-solving skills, and earn better grades. Users can find a wealth of varied content—including tutorials, interactive simulations, visualization exercises, active figures, drawing tools, and more—to address different learning styles.



*Odyssey*<sup>®</sup> is a molecular dynamics force-field engine that accurately portrays the molecular world for introductory and general chemistry classes in colleges and universities. Utilizing pre-built or student constructed molecular simulations, *Odyssey* provides an interactive environment for learning and exploration. The *Chemistry: Human Activity, Chemical Reactivity* integrated print/digital resource makes it easy for students and instructors to be immersed in the molecular world to learn molecular-level concepts like intermolecular bonding, polarity, heat transfer, and other threshold concepts. If your instructor has chosen to bundle *Odyssey* with your text, install the *Odyssey* software onto your computer from the Wavefunction website (wavefun.com) and use the access code provided to access the program.



### Student Solutions Manual

**ISBN-10: 0-17-668863-3**

The **Student Solutions Manual** contains detailed solutions to all odd-numbered end-of-chapter exercises. Solutions match the problem-solving strategies used in the text. Prepared by Jillian Hatnean, University of Toronto, and Mark Vaughan, Capilano University; technically checked by Rabin Bissessur, University of Prince Edward Island.

### Chemistry: Student Activity, Chemical Reactivity Workbook

**ISBN-10: 0-17-658352-1**

Study more effectively and improve your performance at exam time with this student workbook! The *Chemistry: Student Activity, Chemical Reactivity Workbook* focuses on the thinking processes required to succeed. Each chapter of this workbook contains chapter highlights/topic map, study strategies, exercises to strengthen visualization skills, a math skills primer, and suggestions for group study activities. Prepared by Rabin Bissessur, University of Prince Edward Island, and John Chik, Mount Royal University.

### Integrated Media on the CHACR Interactive Tutorial and Visualization Resources Website

[www.nelson.com/chemistry2ce](http://www.nelson.com/chemistry2ce) The digital resources in the *Chemistry: Human Activity, Chemical Reactivity* project are an integral part of the learning experience, bringing the case studies and molecular-level concepts to life. A margin icon indicates when a particular resource on the website is most relevant to extend your understanding, with an animation, simulation, video of a reaction, an interactive tutorial with feedback, or a practice exercise. Each type of resource—*Molecular Modelling, Taking It Further, Think about It, Background Concepts*—has a brief description indicating what you will do in the activity. Learning is an *active* process, and educational research indicates that learning is more efficient if you *process* and *apply* ideas while you read about them.

Access to the website is included with the purchase of a new text. Simply register once, using the sign-on card accompanying this text, and you have full access to the most comprehensive collection of e-resources for any chemistry textbook on the market.

## Acknowledgments

We have learned so much from each other as co-authors over the eight years of working together. During that time, and over our entire careers, we have been continuously inspired and re-energized by our students, for whom we have created this learning resource. Colleagues at our universities, in our countries, and internationally, listed below, have contributed ideas, advice, critique, and peer review of different parts of this resource. We have been fortunate to draw on the experience, advice, and thoughtful review of Editorial Advisory Boards of leading university chemistry educators in Canada, Australia, and New Zealand.

We highlight the seminal contributions made by Jurgen Schnitker and his colleagues at Wavefunction, Inc. They have supported this project from its inception with the molecular dynamics *Odyssey* software, and advised over many discussions the best ways to build robust mental models of dynamic molecular systems for general chemistry students. We are also grateful for permission to use figures from *Odyssey* throughout the resource.

The resource package is published by Nelson Education Ltd. for distribution in Canada and internationally. Thank you to Scott Sinex who has graciously provided permission for the use of his Excel spreadsheets to enrich the e-resource material. It has been a true pleasure to share and co-develop a vision with Publisher Paul Fam for an integrated, contemporary package of text and electronic resources that incorporates important pedagogical innovations in teaching and learning chemistry. We are grateful to the amazing team at Nelson, including Publisher Paul Fam, Senior Production Project Manager Imoinda Romain, Marketing Manager Leanne Newell, as well as to Permissions Editor Julie Pratt and Copy Editor Wendy Yano. Thank you to Developmental Editor Mark Grzeskowiak at Nelson for patiently and competently guiding us through the myriad of details needed to bring this to production. Also, without the foresight of Elizabeth Vella, then at Cengage Australia, who co-commissioned the project in 2005, the collaboration among authors and publishers would never have been brought forward.

Finally, we acknowledge individual contributions, as follows.

### Peter Mahaffy

I have been sustained in my work by the daily, concrete support of my family, and offer my heartfelt gratitude for their role in making this vision become real. From writer Cheryl, I keep learning how to make words sing. Reuben, Naomi, and Miriam each inspire in different ways with their integrity, creativity, and love of learning. Brother and fellow chemist Paul has read several chapters and is always willing to talk shop. My love for the world of learning and teaching has been nourished by my mother and teacher, Arlena Mahaffy. My approach to learning and teaching has been shaped by many passionate and compassionate educators: If I single out only a few, they might be PhD mentor Mike Montgomery, Renaissance chemist Roald Hoffman, King's colleague Brian Martin, and University of Alberta colleague Margaret-Ann Armour.

### Bob Bucat

For enriching me as an educator, Alex Johnstone (Scotland) and Peter Fensham (Australia) deserve my reverence. Most influential of all of my professional colleagues in my career and in this project is the late Professor Sir Noel Bayliss, my PhD supervisor and mentor of so many years ago, who demonstrated to me so often that it is possible to think like a molecule. How valuable this has been to me as a teacher! Above all, I dedicate my contribution to Lucinda, Sally, Jacqueline, Bob, Ben, and Michael, as well as their children (my 13 grandchildren) for the fact that I have spent so much less time with them than I would have liked. I will make it up.



## Roy Tasker

I would like to dedicate my contribution to my family—Diane, Ken, and Skye—for their loving support and understanding for my all-too-often mental and physical absences from their lives during this project.

I would like to acknowledge three mentors who have influenced my approaches and priorities used in this project: Alex Johnstone (formerly at the University of Glasgow), Peter Atkins (formerly at Oxford University), and Loretta Jones (formerly at the University of Northern Colorado).

Mark Williams has been a valued colleague who has shared the load of testing so many of our interactive resources with our chemistry students.

## First Edition Editorial Advisory Board Members and Reviewers

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# THE AUTHORS

**Peter Mahaffy's** passion is for helping undergraduate students and others see the intricate web that connects chemistry to so many other aspects of life and to the health of our planet. After receiving his PhD in Physical Organic Chemistry from Indiana University, he moved to Canada where he is now Professor of Chemistry at the King's University College in Edmonton, Alberta, and Co-Director of the King's Centre for Visualization in Science. Peter collaborates regularly on research with undergraduate students in the areas of chemistry education, visualization in science, organic chemistry, and environmental chemistry. His recent focus is on the effective use of rich contexts and guided inquiry approaches to facilitate learning of chemistry. He is past-chair of IUPAC's Committee on Chemistry Education (CCE) and co-led the team that obtained UN designation of 2011 as an International Year of Chemistry. Recent teaching awards include the *Chemical Institute of Canada National Award for Chemistry Education*, the *3M National Teaching Fellowship*, the *ACS James Flack Norris Award for Outstanding Achievement in the Teaching of Chemistry* and the *IUPAC CCE Award for Distinguished Contributions to Chemistry Education*.



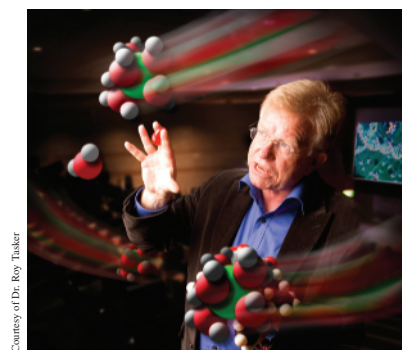
Courtesy of Dr. Peter Mahaffy

**Bob Bucat** is an Honorary Teaching Fellow at the University of Western Australia. After attaining a PhD in physical chemistry, his research interests have been related to the challenges of education in chemistry at the tertiary level. His research and teaching interests have centred on strategies to encourage thinking, the importance of language used (in word forms, symbolic forms, and graphics), and the challenges of visualization of molecular structures, and probabilistic and dynamic processes in reaction mixtures. He is a devotee of the notion of pedagogical content knowledge: both content knowledge and pedagogical knowledge are necessary for good teaching, and each concept and topic has specific pedagogical challenges that demand specific teaching strategies. Bob has been a titular member of the IUPAC Committee on Teaching Chemistry, and a member of the National Committee for Chemistry of the Australian Academy of Science. He is a winner of awards for teaching excellence at UWA. He has also been awarded the *Medal of the Chemical Education Division of the Royal Australian Chemical Institute*, the Australian Government's *Carrick Medal*, the inaugural *Fensham Medal* of the RACI, as well as the IUPAC Committee on Chemistry Education *Distinguished Contributions to Chemistry Education Award*. In 2011, he was declared by the RACI as a *Living Luminary of Australian Chemistry*.



Courtesy of Dr. Bob Bucat

**Roy Tasker** is Professor of Chemistry Education at the University of Western Sydney (UWS), and has been teaching first-year university students since 1985. With a PhD in synthetic inorganic chemistry from the University of Otago, and post-doctoral appointments at the Universities of Tasmania and Adelaide, he became interested in chemical education, and in particular, developing students' mental models of the molecular world. This led to the development of an integrated suite of molecular-level animations in the *VisChem* project in the early 1990s. These resources are still used at secondary and tertiary levels all over the World. During a three-year secondment with *CADRE design*—a multimedia production company—he gained experience in developing interactive multimedia resources to complement and supplement nine university-level chemistry and biochemistry textbooks. Since 2000, his research group has worked with students to study what and how students learn from molecular animations and simulations, and on this basis, developed the *VisChem Learning Design*. In 2011, he received the *Prime Minister's Award for Australian University Teacher of the Year*, and in 2002, the *Royal Australian Chemical Institute Chemical Education Division Medal*.



Courtesy of Dr. Roy Tasker

This learning resource adapts from and builds on the proven resources of two U.S. textbooks that have successfully served well over a million chemistry students: *Chemistry & Chemical Reactivity* by the author team of **John Kotz** (State University of New York), **Paul Treichel** (University of Wisconsin–Madison), and **Gabriela Weaver** (Purdue University); and *Fundamentals of Organic Chemistry* by **John McMurry** (Cornell University).



# Human Activity, Chemical Reactivity



Courtesy of Professor Bob Hicart

## Outline

- 1.1 Chemistry: Human Activity, Chemical Reactivity
- 1.2 Harnessing Light Energy and Exciting Oxygen
- 1.3 Where There's Smoke, There's Gavinone
- 1.4 Chemical Reactivity, Your Activity

## 1.1 Chemistry: Human Activity, Chemical Reactivity

Read the title of this textbook once again: *Chemistry: Human Activity, Chemical Reactivity*. As you study chemistry this year, the authors hope you will obtain a much better understanding of how human activity and chemical reactivity are woven together in every aspect of modern life. You'll be in good company! Stressing that education in and about chemistry is critical to address challenges such as global climate change and sustainable supplies of clean water, food, energy, and medicine, the United Nations declared 2011 to be the International Year of Chemistry. Activities took place around the world to increase understanding of chemistry and how the tools of chemistry are at work in almost every aspect of modern life.

This first chapter tells the stories of two people who carry out research in chemistry to improve our world. You would not recognize them on the bus or in the supermarket as chemists. They are simply curious, hard-working people who use logic and creativity as they work with a research team to design and interpret experiments.

First we'll meet David Dolphin, a Canadian chemist who has designed and made new substances that have improved the quality of life for over a million people suffering from cancer or eye disease. Then we'll meet Gavin Flematti, an Australian chemist who, while he was a postgraduate student, identified a compound in smoke that causes plant seeds to germinate after a forest fire. He then found a way to make this compound in the laboratory.

You'll see with these two people that the work chemists carry out is challenging for many reasons, not least of which is that the particles they study—particles that make up everything in our world—are too small for us to see directly. So chemists develop and use instruments to extend their vision and to understand how the things we observe fit with molecular-level explanations.

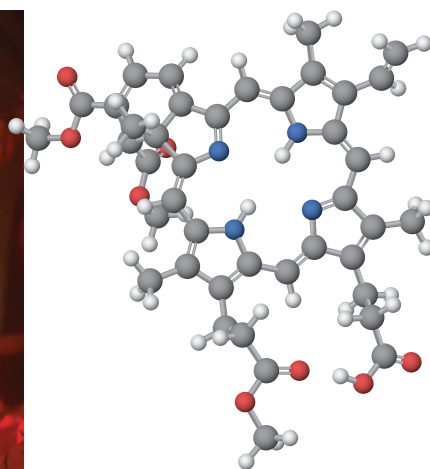
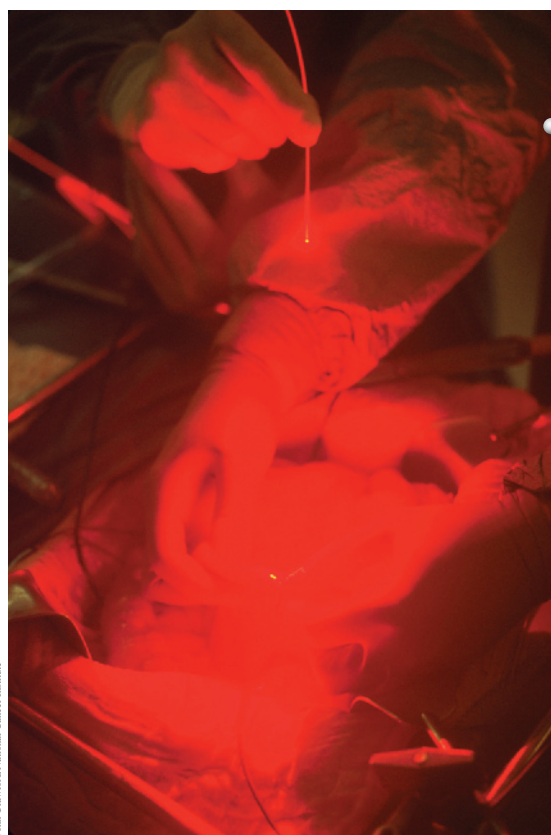
As in so many areas of modern chemistry, in both of these stories, the interaction of electromagnetic radiation with matter plays a critical role. In the first case, visible light from a laser triggers the production of molecules that selectively destroy undesirable cells in

body organs. In the second, selective absorption of electromagnetic radiation is the key to understanding the three-dimensional structures of newly discovered molecules in smoke.

**Spectroscopy** is the study of characteristic patterns of absorption of electromagnetic radiation, used to identify substances and to provide information about the structures of their molecules. **Chromatography** is the science of separation of compounds from complex mixtures. These two techniques—part of an array of instrumental methods that have revolutionized the practice of chemistry—are at the heart of the stories about the success of these two people and the significance of the research they have carried out.

On your first reading, you should not expect to completely understand the chemistry related to these two stories. In Section 1.4 and later in the text, we return to the concepts introduced here. Through these stories and the discussion questions that follow, we hope you will appreciate that advances in chemistry happen today, and that they can improve life for humans and the environment—the very reasons the United Nations declared an International Year of Chemistry. The advances described in this chapter and this book did not take place overnight, and they required sound knowledge of chemistry and other disciplines. They were made by logical thought processes and careful experiments, carried out by teams of creative people—people like those you meet every day. Perhaps most of all, we hope you appreciate that you, too, could participate in significant research in chemistry or other sciences. You might want to read these stories again later for an even deeper appreciation.

## 1.2 Harnessing Light Energy and Exciting Oxygen





We live each day in a tropospheric atmosphere of oxygen and nitrogen molecules, and move around on the earth's crust, made mostly of oxygen atoms in combination with other elements such as silicon, nitrogen, carbon, and sulfur. Oxygen atoms are in the middle of  $\text{H}_2\text{O}$  molecules, which comprise the substance water, which in turn covers three-fourths of the surface of our planet. Without oxygen, life as we know it would be impossible. Molecular oxygen,  $\text{O}_2$ , makes up one-fifth of the air that we breathe. Our brains consume about 20% of the molecular oxygen that we breathe in. This oxygen fuels numerous processes, including the electrical circuits that enable us to read and to think about our molecular world.

And yet, many forms of oxygen are highly toxic to human cells, including one form of molecular oxygen.

## Two Energy States of Oxygen Molecules

How can molecular oxygen ( $\text{O}_2$ ) be both essential to life and highly toxic? This riddle can be answered if we realize that  $\text{O}_2$  can exist in different forms or energy states. This story is about two of those states: *singlet* oxygen and *triplet* oxygen. The terms *singlet* and *triplet* refer to differences in the energy levels of the electrons of  $\text{O}_2$  molecules, explored further in Chapter 10. Those differences in the energies of the electrons of  $\text{O}_2$  molecules cause a profound difference in chemical reactivity—the difference between life and death for cells.

In triplet  $\text{O}_2$ , the electrons in the  $\text{O}_2$  molecules are in their lowest energy state (the *ground state*, [>>>Section 8.5]). This is the oxygen we breathe. The electrons in singlet oxygen molecules are in higher energy (excited) states. Singlet  $\text{O}_2$  molecules can be formed when energy is transferred to triplet  $\text{O}_2$  molecules as they collide with other “excited” molecules. Because singlet  $\text{O}_2$  is exceptionally reactive, it doesn't last long.

While triplet  $\text{O}_2$  in the air we breathe fuels life, singlet  $\text{O}_2$  has very different physical properties and chemical reactivity. It bleaches coloured materials and polymers, and is highly toxic to dividing human cells. Singlet  $\text{O}_2$  can be produced in laboratories as well as in nature. Respiration in animals and photosynthetic reactions in plants produce small amounts of singlet  $\text{O}_2$ , and chemists have learned a lot about how photosynthetic microbes and plants respond to the production of this toxic substance.

## Chemotherapy and Photodynamic Therapy

Toxic or poisonous substances can sometimes be used to advantage in medicine. **Chemotherapy** is the use in medicine of substances that are selectively toxic to malignant cells or a disease-causing virus or bacterium. Because of its toxicity to dividing cells, singlet  $\text{O}_2$  has found a role as a chemotherapeutic agent. An important chapter in the singlet  $\text{O}_2$  story is the work of Professor David Dolphin from Canada's University of British Columbia. He and his research collaborators ► created Visudyne™, one of the world's most successful ophthalmic products. Since 2000, Visudyne™ has been used to treat more than a million people in 75 countries for age-related macular degeneration (AMD), the leading cause of vision loss for people over the age of 50 in the Western world.



Courtesy of Dr. David Dolphin

David Dolphin with his research group, who have come from around the world. In recognition of the impact of his work, Dolphin received Canada's top science prize in 2005. He has also been appointed an Officer to the Order of Canada and designated a “hero of chemistry” by the American Chemical Society. ▲

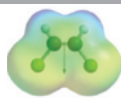
*“I get my kicks out of solving problems, whether they're basic ones or more applied . . . I know from my own graduate students that they're very excited about getting involved in research that might eventually benefit humanity.”*

**David Dolphin**

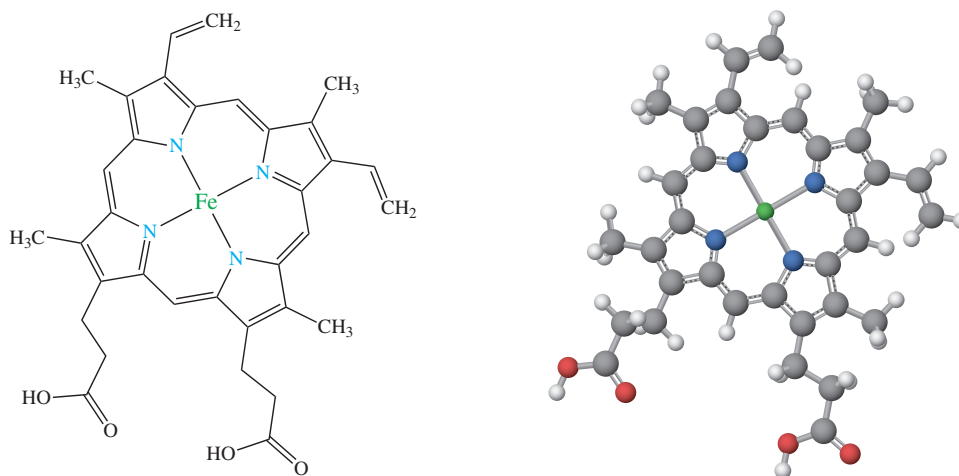


### Molecular Modelling (Odyssey)

**e1.1** Examine a simulation of the heme group, separately and embedded in hemoglobin.



**FIGURE 1.1** Two representations of a heme group from a hemoglobin molecule. The iron atom (Fe, green) is in the centre of the large porphyrin ring, identified by its four nitrogen atoms (N, blue).



The light-absorbing properties of porphyrins also make them good **photosensitizers**, substances whose electrons can be excited by absorbing light of appropriate wavelength. They can then transfer their extra energy through molecular collisions to substances such as triplet  $O_2$ —producing singlet  $O_2$ . Dolphin had the imagination to see how porphyrin photosensitizers and light might work together with oxygen in medicine.

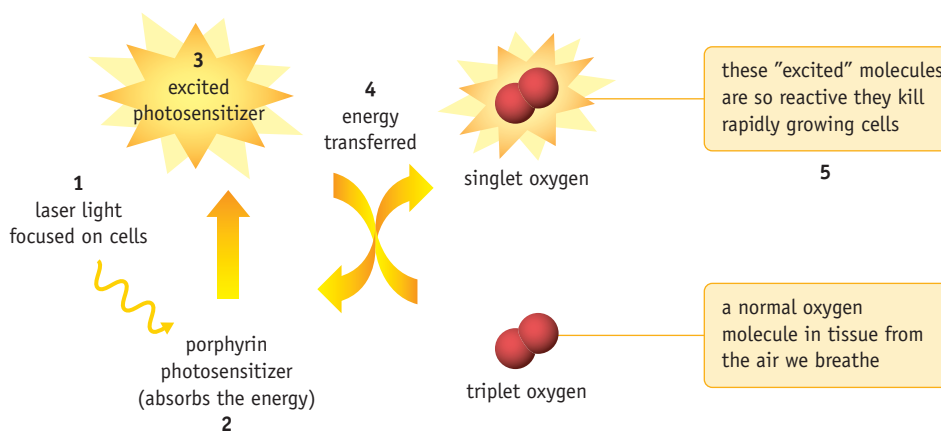
But Dolphin wasn't the first to think about photodynamic therapy. His breakthroughs built on many years of work by chemists in other countries. The basic technique was first developed in 1972 at the Roswell Park Cancer Institute in Buffalo, New York. PDT is a minimally invasive medical treatment with three components that work together: (a) the administered drug (a photosensitizer), (b) light to excite the photosensitizer molecules, and (c) triplet  $O_2$  in tissue (Figure 1.2). Excited photosensitizer molecules transfer energy to triplet  $O_2$  in tissue, converting some of it to singlet  $O_2$ , which can kill rapidly growing cancer cells. ◀

### Think about It

**e1.2** Watch a video illustrating the mode of action of photodynamic therapy.



**FIGURE 1.2** Steps in making a singlet oxygen molecule. Laser light energy (1) is absorbed by a photosensitizer molecule (2) in a cell, converting the molecule to its excited state (3). Energy is transferred (4) to a nearby triplet oxygen molecule to form a "lethal" singlet oxygen molecule (5).



In Dolphin's PDT work, the photosensitizer is a porphyrin-containing compound, which is administered to the site of rapidly growing cells. The light source is usually a red light from light-emitting diodes or a laser diode.

Dolphin and his research team initially developed porphyrin PDT treatment for various cancers on or near the surface of the skin. The patient is given a dose of a photosensitizer or a substance that can be metabolized by the body into a photosensitizer. The drug might be injected at the site of the cancer or it might be designed to attach itself to *lipoprotein* molecules in the bloodstream so that it is transported to the affected area. ► After waiting an appropriate amount of time, the physician applies red light to the target site. In one second, one molecule of Visudyne™ is able to make more than one million molecules of singlet O<sub>2</sub>. The singlet O<sub>2</sub> that is formed lasts for only about a microsecond ( $1 \times 10^{-6}$  s), but during that time it damages or destroys the rapidly growing cancer cells.

It is important that, as far as possible, singlet O<sub>2</sub> is produced only at the site of the cancer, or otherwise healthy cells may be killed. Since the **half-life** ( $t_{1/2}$ ) of the photosensitizer in the human body is about five hours, a patient undergoing PDT must be careful about exposure to sunlight after treatment to avoid singlet O<sub>2</sub> production in other parts of the body where small amounts of the photosensitizer might still be present.

### Unexpected Results: Effect on Vision

The development of Visudyne™ came from an unexpected turn in Dolphin's PDT cancer research. Patients undergoing PDT clinical trials for cancer reported beneficial effects on their vision. Researchers learned that some porphyrin photosensitizers had the unexpected effect of closing down abnormally growing blood vessels in the eyes of patients who also suffered from the most common “wet” form of age-related macular degeneration. ► Wet AMD is caused by the growth of an abnormal tangle of new blood vessels under the macula in the retina. These vessels then leak fluid and cause scar tissue, leading to the rapid loss of sight. ►►

Visudyne™ is an equal mixture of two porphyrin-containing photosensitizers whose molecules are **isomers**, and have the structures shown in Figure 1.3.

The normal protocol for treating AMD with Visudyne™ can now be carried out in a doctor's office. The photosensitizer drug is administered intravenously, where it attaches to lipoprotein molecules and is carried selectively to the abnormal vessels in the eye. After five minutes, a red laser is shone into the patient's eye through a microscope for just over one minute. This excites the photosensitizer molecules, which then transfer their excess energy to triplet O<sub>2</sub>, producing singlet O<sub>2</sub> to destroy the abnormal blood vessel cells.

### Finding the Right Combination of Photosensitizer and Light

It took years of research by Dolphin's research team to design and then synthesize Visudyne™. The first photosensitizer used by Dolphin's group was already available in the form of the drug Photofrin from the Roswell Institute, but it was a mixture of a countless number of compounds—most of which are not active in treating AMD. It was very difficult to reproduce the production of different batches of such a complex mixture. Photofrin had a much longer half-life in the body, so patients had extreme sensitivity to the sun for a period of time, and exciting the drug required light in the blue region of the visible spectrum. Since blue light does not penetrate far into human tissue, Photofrin is limited to treating only conditions on or very close to bodily surfaces.

In designing a new photosensitizer Dolphin knew that naturally occurring porphyrin compounds readily absorb light, but found that the iron atoms in the centre of the porphyrin rings in heme must be removed for PDT applications, as they prevent singlet O<sub>2</sub> from forming. When Dolphin's research team set to work to design and make their own porphyrin compounds in the lab, they first made compounds that were slightly different than the mixture of two compounds in Figure 1.3. At the bottom of each structure, shown in red, are two **functional groups** [>>>Section 3.11], one of which is a **carboxylic acid**, and one an **ester**. In the first photosensitizer they designed, both of these groups were esters, but they found that not nearly enough of the drug dissolved in water, so they

*Lipoproteins* are molecules that are combinations of proteins and fats, and are responsible for transporting fats and fat-like substances like cholesterol through the blood.



Advanced age-related macular degeneration. ▲

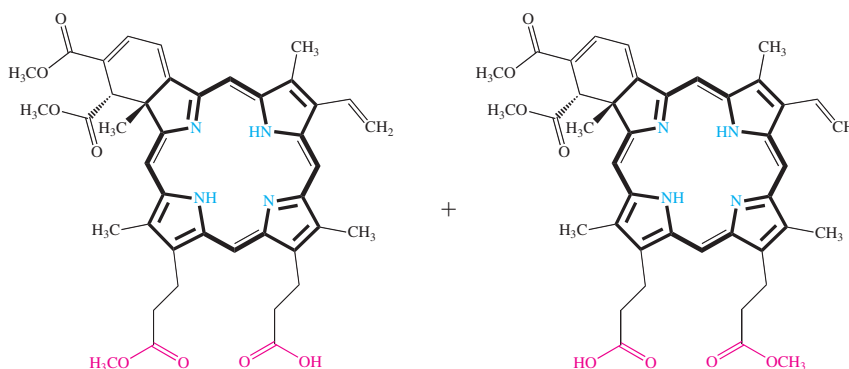


▲



Normal vision and age-related macular degeneration. ▲

**FIGURE 1.3** The two photosensitizer molecules that make up Visudyne™. The cyclic porphyrin rings are highlighted, and each bend in the structure in this representation symbolizes the presence of a carbon atom. Two molecules with the same formula but a different arrangement of atoms, such as these two, are called *isomers* [>>>Section 4.5]. Can you spot the subtle difference between the two isomers?



replaced one of the ester groups with a carboxylic acid group to increase solubility. This change proved to give the right combination of water solubility and high activity as a photosensitizer. And unlike Photofrin, red light is needed to excite the Visudyne™ molecules, and red light penetrates somewhat further than blue or green light into human tissue.

### Next Steps for PDT and Porphyrins

Treating a complex disease like AMD requires ongoing research and development. Chemists are now working to improve many aspects of PDT, focusing especially on the design of photosensitizers and sources for the visible light needed to excite them. Efforts are directed toward making new single-compound photosensitizers capable of strongly absorbing light of a specific wavelength that is not absorbed by blood. Other research goals are to develop sources of light that will penetrate more deeply into tissue without causing damage. Also needed are better methods of formulating and administering photosensitizers (or compounds that can be converted into photosensitizers) to patients. Computer modelling studies help chemists predict how to modify portions of photosensitizer molecules to improve their selective accumulation at cancer sites, and nanoscale substances are being custom-made to transport photosensitizers, increase their efficiency, and reduce side effects of PDT.

Since Visudyne™ was first made and approved, alternatives for treating AMD have been found that work in entirely different ways to treat macular degeneration. But there is still a significant market for the drug around the world, and new protocols, which combine Visudyne with other drugs, are also being tested.

Understanding porphyrin chemistry has now led to a remarkable range of applications. In medicine, PDT is now also being used to treat quite a range of cancers, to facilitate wound healing, treat dental disease, inactivate mammalian viruses and bacteriophages, and treat water and sewage. And research groups are now trying to use the light-absorbing ability of porphyrins to create inexpensive electrodes for fuel cells [>>>Section 7.1], to make catalysts to produce ammonia gas from nitrogen gas [>>>Section 13.1], and to convert water into hydrogen gas and oxygen gas.

## 1.3 Where There's Smoke, There's Gavinone





Throughout this textbook you'll read about reactions, compounds, and processes named after the people who discovered them. But can you imagine having a compound that might be worth millions of dollars named after you? That happened recently to an Australian chemistry student who discovered that trace amounts of a previously unknown compound in the smoke from wood fires causes plant seeds to start growing. The student's name is Gavin Flematti, and for a time the new compound was named Gavinone in his honour by the botanists on his research team. ▶

The task wasn't easy. Gavinone is only one of thousands of compounds found in wood smoke, yet Flematti and his collaborators proved that very low concentrations (less than 1 part-per-billion) of this compound can cause seeds to germinate.

His discovery is important. Researchers knew that a compound causing seeds to germinate would be of great interest to agricultural and chemical industry. It could be used to control weeds, possibly saving farmers around the world millions of dollars. It might also help regenerate native plant species without the use of fire, or help plants grow in reclaimed soil on top of abandoned mine sites. Flematti and his research supervisors knew that they needed to start by understanding at the molecular level what causes germination after fires in nature. Eventually they might apply that knowledge to make substances in the laboratory that could be applied to seeds or to soil.

Let's try to understand the steps Flematti and his research team took in making this breakthrough. It took years of sleuthing as an undergraduate and then as a PhD chemistry student to isolate this single compound from smoke, prove that it causes seeds to germinate, identify the three-dimensional structure of its molecules, and then synthesize it in the laboratory.

## How Do Seeds Germinate?

First, they needed to understand some plant biology. How do plant seeds survive in seed packets or on the ground and then germinate? Seeds can remain dormant until environmental conditions are suitable for the growth of the plant through the vulnerable seedling stage. Seed germination begins with the uptake of water by dry seeds. Then, a part of the embryo called the *radicle*, which develops into the primary root, penetrates the protective coating. This is a desirable characteristic for plants in nature, and can also be beneficial in agriculture. For example, wheat farmers often sow seed in dry land prior to seasonal rains, knowing that germination won't occur until the soil receives enough moisture. Seeds on the heads of grain also must remain dormant so that they do not germinate before harvesting.

On the other hand, the seeds of some crops remain dormant after planting, and not all of them germinate when the farmer or nursery owner would like. Crop growers would place great value on a substance that promotes germination of all seeds at the same time, and such understanding could contribute to strategies to address severe food shortages in parts of the world. For example, it would be very useful if weed seeds in the ground could be made to germinate before the main crop is sown. The weed plants could then be sprayed with herbicide and eliminated as competitors for soil nutrients.

## Where There Is Fire, There Is Smoke

Next, they needed information about fires. It is astonishing to see that, following a major forest fire, a blackened landscape can explode into colour the next spring. Seed germination was thought to be due to heat from the fire cracking open the seeds lying dormant in the ground. Heat is indeed important for some plants, but scientists in South Africa, Australia, and North America had shown that smoke alone, in the absence of heat, can also cause many seeds to germinate. Smoke is a very complex chemical soup, composed of many thousands of compounds. ▶ Throughout history, being the first to make an important discovery has often been a strong motivating force in science. Flematti and his collaborators, along with competitors from several other countries, set out on a race to be the first to identify which bioactive compound or compounds in smoke promote germination.



Courtesy of Gavin Flematti. Photo by Fran Cox.

Gavin Flematti behind a poster promoting his work. ▲

Courtesy of Mr. Brian Wiens, Head of Air Quality Science Unit, Environment Canada



Smoke from a forest fire in the Canadian Rockies. ▲

## Where There's Smoke, There's Chemistry

Smoke from a wide variety of plant materials was shown earlier to be effective in causing seeds to germinate, but little was known about why this worked. Somehow, compounds in smoke must interact with others in seeds. Flematti did know that the compounds in smoke responsible for germination dissolve more easily in organic solvents than in water. This suggested that the active substances are probably one or more of the millions of **organic compounds** [>>>Section 3.6] whose molecules are made of a framework of carbon atoms with hydrogen atoms attached, and often include oxygen, nitrogen, or several other types of atoms. Although a number of components of smoke had been previously identified by other researchers, none of these promoted germination. The bioactive compound was like a “needle in the haystack,” hiding among the thousands of compounds in smoke.

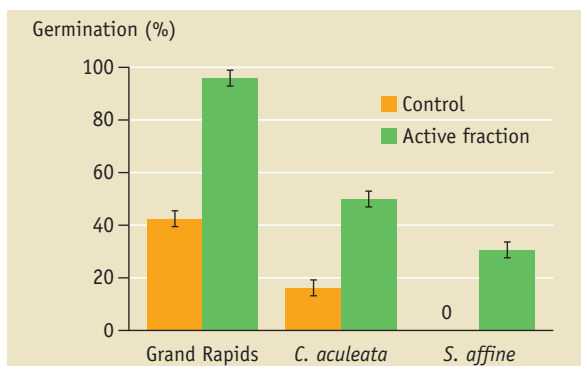
## How to Find the “Needle in the Haystack”

The challenge Flematti faced is common in **natural products chemistry**, the branch of chemistry that studies compounds produced by living organisms. The general approach to finding the bioactive compound from so many possibilities involves several steps and a great deal of patience.

First, Flematti would need a reproducible source of the compounds in smoke from wood fires. Then, he would need to collect the complex mixture of compounds from that smoke, and determine if it helped seeds germinate. Since there are thousands of possible compounds that could be responsible, he would need to use repeated *chromatographic* separation techniques to divide the compounds into several groups, each of which contains fewer compounds. On each of those smaller groups of compounds, he could then use screening methods, called **bioassays**, to see if that group contained the active compound(s). This process of separation and bioassays would need to be repeated over and over for the “haystack” containing the “needle” to become smaller and smaller.

If a single compound could be isolated and shown to cause the bioactivity, the next challenge would be to determine its identity. Flematti would need to use powerful methods of structural determination, such as **mass spectrometry** [>>>Chapter 3], **nuclear magnetic resonance (NMR) spectroscopy**, and X-ray crystallography [>>>Chapter 9], to determine the composition and three-dimensional structure of the molecules of that compound. Finally, once the molecular structure of the substance was known, he might try to synthesize the same compound in the laboratory. This would help to prove that its structure was correct, and provide larger amounts for further testing and commercial use.

Chromatography is used to separate compounds from mixtures. Spectroscopic techniques, based on the way different molecules interact with electromagnetic radiation, are powerful tools for identifying compounds. A bioassay is a test for biological activity.



**FIGURE 1.4** Bioassay effectiveness. Percent germination of Grand Rapids lettuce seeds and two Australian native plant seeds in response to smoke from burning filter paper (cellulose). Filtered water (with no smoke components) was used for the control experiments.

Source: Flematti et al., *Plant and Soil*, 263: 1–4, 2004.

## Producing and Testing Wood Smoke

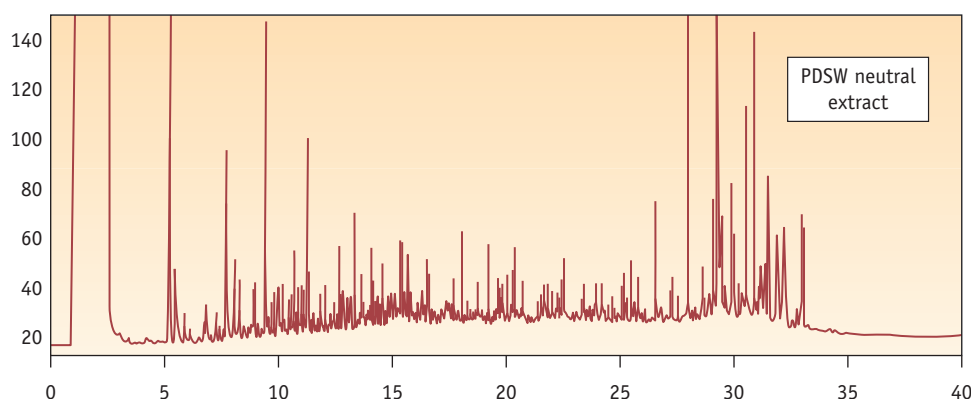
Flematti and his collaborators burned laboratory filter paper as a source of smoke which is passed through water to make “smoke water.” This seemed reasonable, since filter paper is mostly cellulose, the primary structural component of all green plants. They used a rapid bioassay technique developed at the University of Natal in South Africa to see if smoke caused germination. When smoke water was applied to the Grand Rapids variety of leaf lettuce seeds kept in the dark, germination took place within 24 hours. Only 45% of the seeds germinated in absence of smoke (called a “control” trial), while 90% germinated with smoke water application. Figure 1.4 shows their finding that these lettuce seeds and seeds of some Australian native plant species responded to smoke compounds.

They then knew that the active compound is found in burning cellulose, which is only one of many compounds in plants. This told them which “haystack” to start looking in.



## Repeated Separations and Bioassays

Now the part of the task requiring the greatest patience—narrowing down the many possible compounds that might be causing the seed germination. Flematti used **extraction** techniques to separate the complex mixture of compounds in smoke into groups of compounds or fractions based on their acid/base and solubility properties. A bioassay was then used on each of those fractions to see if they contained the bioactive compound(s). Several types of *chromatography* were then used one after the other on the bioactive fractions, to create smaller and smaller groups of compounds. To give you an idea of the complexity of the problem, Figure 1.5 shows one of Gavin's gas chromatogram charts indicating the number of compounds found in just one fraction from plant-derived smoke water. Each "peak" or upward spike in the chromatogram represents a different chemical compound. One of these would eventually prove to be Gavinone. But which one?



**FIGURE 1.5** Gas chromatogram of neutral fraction from plant-derived smoke water. Each peak in this chromatogram corresponds with a particular compound after it is pushed through the column by an unreactive gas. The horizontal axis is the time (minutes) before exit of each compound from the column. The vertical axis indicates the response of the detector at the exit, indicating the relative amount of substance reaching the detector at that particular time.

Source: Gavin Flematti.

## Isolating the Bioactive Compound

After many rounds of chromatography separations, Flematti took 5 mg of the most active fraction and yet another solvent mixture. One of these fractions showed only about a dozen compounds. But he had less than 0.2 mg of material to work with in that fraction. That is about the mass of 1/100th of a grain of rice!

So as he had done many times before, back to the beginning again, burning an even larger amount of filter paper and repeating the many separations. This time he obtained a whopping amount of 1 mg (0.001 g) of each of three bioactive fractions, enough to work with using sophisticated instrumental techniques. From one of those fractions, Flematti separated out a single compound, and it was bioactive. The compound had a **molecular weight** of 150. For the first time ever, the compound in smoke causing seed germination had been isolated. The “needle in the haystack” had been found—but its identity, apart from its molecular weight, was still unknown.

## What Is the Bioactive Compound?

As you will see in Chapter 3, a mass spectrometer can reveal the molecular weight of a compound, as well as how it breaks up into smaller pieces called fragments. Those fragments give information about the pattern of connectivity of atoms in each molecule. Large international databases list the fragment patterns in the mass spectra of every compound reported in the research literature. The *mass spectral fragmentation pattern* [>>>Sections 3.9, 3.10] of the active component in smoke did not correspond with that of any other previously known compound. The active compound had never been reported in the chemistry literature before!

Mass spectra indicated a molecular weight of 150, and exact correspondence of the existence of certain isotopes by *high-resolution mass spectrometry* [>>>Section 3.8] showed its formula to be  $C_8H_6O_3$ . From the molecular weight, the mass spectral fragmentation patterns, the wavelengths of ultraviolet light absorbed, its solubilities in different