2009

Sustainability: Energy & Global Chemistry

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Sustainability: Energy & Global Chemistry

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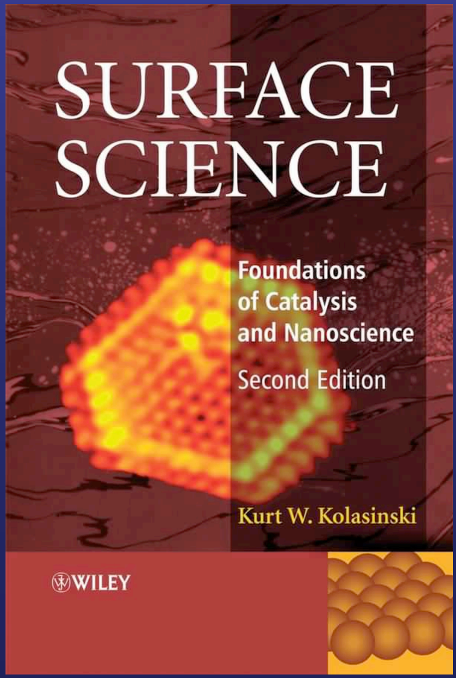
Department of Chemistry



WCU Sustainability Co-ordinator to be appointed

- Presidential Initiatives 2009–2010
  Enable WCU to achieve national and global recognition as a leader in the implementation of green technologies, in sustainable energy, and in the reduction of our carbon footprint.

Too Precious to be Expensive

- Energy
- Water
- Ammonia
- Why do we need energy?
- Why do we need sustainability?
- What does chemistry have to offer?

Sustainability

- An attempt to provide the best outcomes for the human and natural environments both now and into the indefinite future.
- Organizing human activity so that society, its members and its economies are able to meet their needs and express their greatest potential in the present as well as the future.

Why do we need energy and why is it so important for sustainability?

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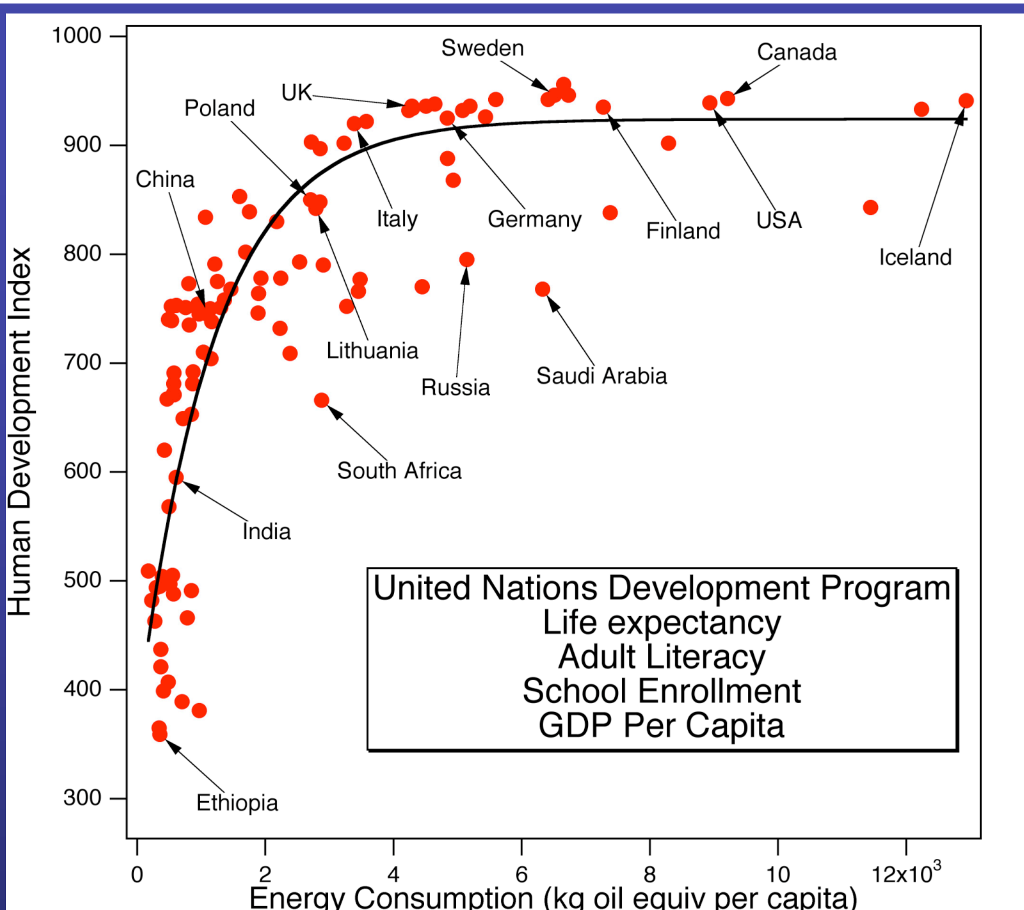

Rank	Country	HDI
1.	Norway	956
2.	Sweden	946
	Australia	946
4.	Canada	943
5.	Netherlands	942
	Belgium	942
7.	Iceland	941
8.	USA	939
9.	Japan	938
10.	Ireland	936
	Switzerland	936
	UK	936
13.	Finland	935
14.	Austria	934
15.	Luxembourg	933
16.	France	932
	Denmark	932
17.	New Zealand	926
18.	Germany	925
19.	Spain	922
20.	Italy	920

- Strong correlation between HDI consumption
- To elevate Developing World to s requires equivalent of 148 Mbbl/
- Current production = 84 Mbbl/day
  - Kolasinski, *Curr. Opin. Solid State Mater. Sci.* **2006**, *10*, 129

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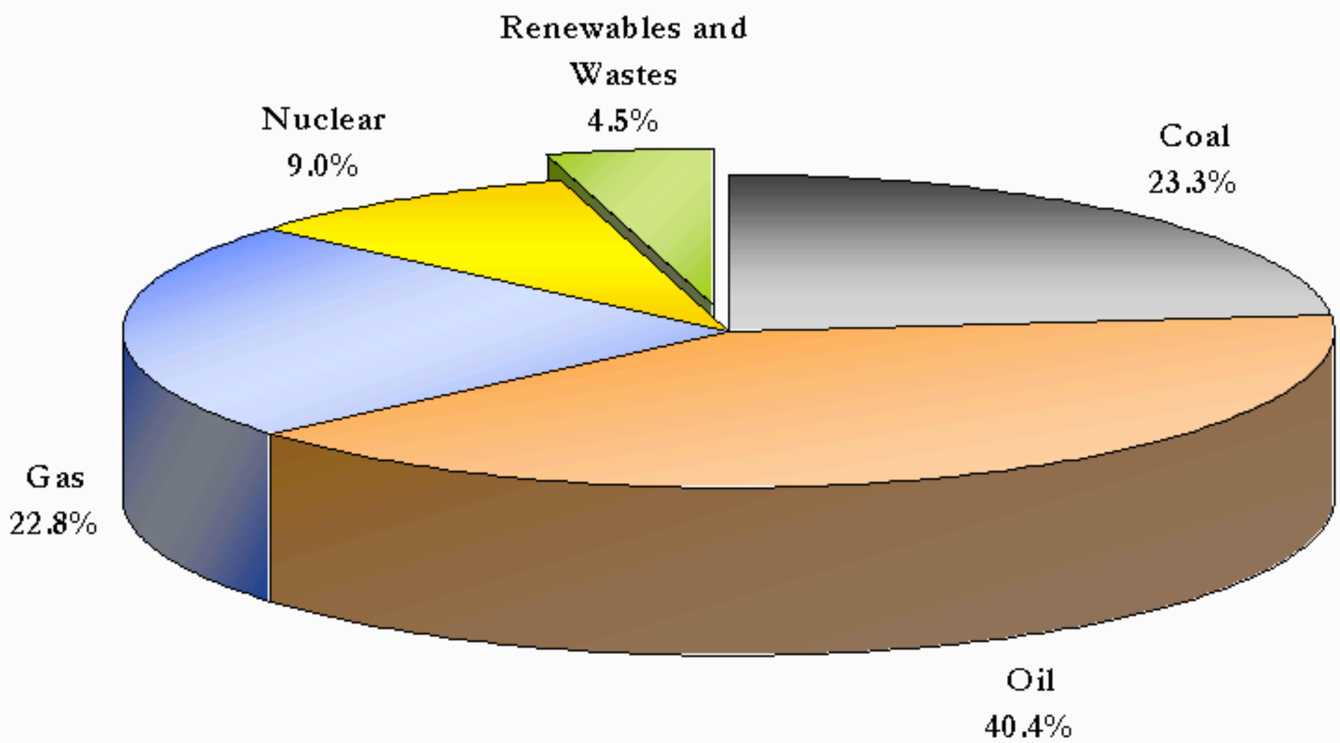
Without sustainable energy sources American and World economic development will cease and conflict will increase

Oil Reserves and Demand

- Proven reserves 21.317 B bbl
- US consumed 7.117 B bbl of oil in 2008
- This amounts to a 3 year supply if we relied on domestic sources

United States - Shares of TPES 2003



Source: IEA Energy Statistics - Copyright: IEA/OECD
Access to detailed data for almost all fuels for both OECD countries and over 100 other countries is available through the IEA website at: http://www.iea.org/statistics

Trends in Supply/Demand

- US energy consumption growing faster than domestic production
- World demand growing >2%/year
- Old wells produce more slowly (–12%/year)
  - US: 5.5 M bbl/day, 10 bbl/day/well
  - Saudi: 10.4 M bbl/day, 10000 bbl/day/well
- Sweet oil disappearing
- Heavy oil consumes gas/water

Geography of Consumption
EIA 2008

	Country (2008)	Population millions	Reserves B bbl	Consumption M bbl/day	Consumption bbl per capita	Imports M bbl/day
1	China	1333	16.00	7.850	2.15	3.88
2	India	1169	5.63	2.940	0.92	2.06
3	USA	307	21.32	19.500	23.18	10.98
4	Indonesia	230	4.37	1.160	1.84	0.11
5	Brazil	192	12.18	2.520	4.79	0.12
6	Pakistan	167	0.29	0.390	0.85	0.32
7	Bangladesh	162	0.03	0.091	0.21	0.09
8	Nigeria	155	36.20	0.290	0.68	-1.88
9	Russia	142	60.00	2.900	7.45	-6.89
10	Japan	128	0.06	4.780	13.63	4.65
11	Mexico	108	11.65	2.130	7.20	-1.06
12	Philippines	92	0.14	0.320	1.27	0.30
13	Vietnam	86	0.60	0.288	1.22	-0.03
14	Germany	82	0.37	2.570	11.44	2.42
15	Ethiopia	79	0.00	0.037	0.17	0.04
16	Egypt	77	3.70	0.700	3.32	0.07
17	Iran	74	138.40	1.760	8.68	-2.42
18	Turkey	72	0.30	0.680	3.45	0.63
19	DR Congo	66	0.18	0.011	0.06	-0.01
20	France	65	0.12	1.990	11.17	1.92
21	Thailand	64	0.46	0.940	5.36	0.58
22	UK	61	3.60	1.710	10.23	0.13
23	Italy	60	0.41	1.640	9.98	1.48
24	Myanmar	50	0.05	0.041	0.30	0.02
25	S Africa	49	0.01	0.583	4.34	0.39

- Per capita consumption extremely unequal
- Economic development in 3rd world will lead to massive increase in energy demand
- China & India now major importers
- In 2005 both UK & Indonesia became net importers

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Oil Production & Consumption

EIA 2008

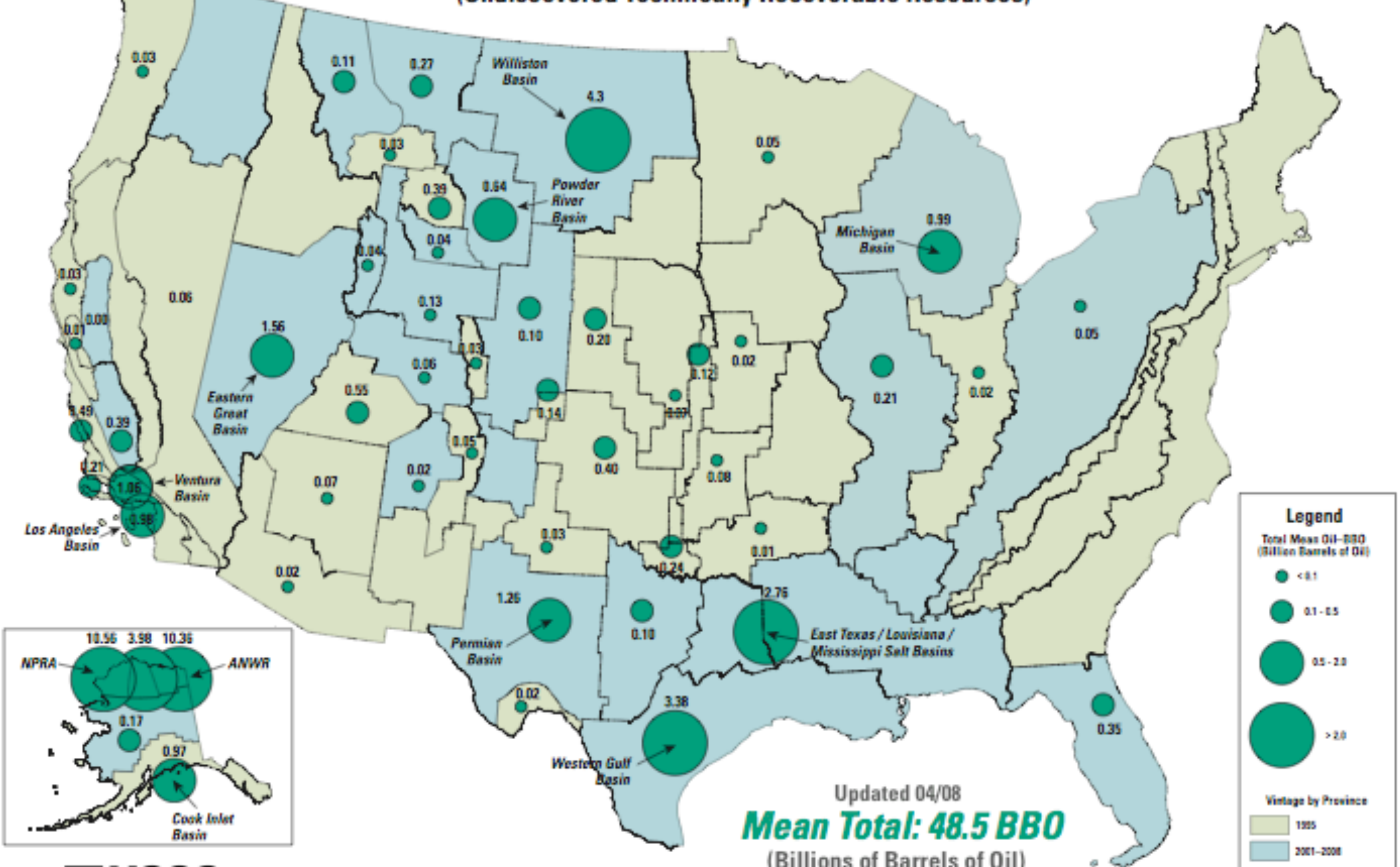
	Reserves	B bbl	Production	M bbl/day	Consumption	M bbl/day	Imports	M bbl/day
1	Saudi	266.8	Saudi	10.78	USA	19.50	USA	10.98
2	Canada	178.6 (>95% oil sand)	Russia	9.79	China	7.85	Japan	4.65
3	Iran	138.4	USA	8.51	Japan	4.78	China	3.88
4	Iraq	115.0	Iran	4.17	India	2.94	Germany	2.42
5	Kuwait	104.0	China	3.97	Russia	2.90	S Korea	2.14
6	UAE	97.8	Canada	3.35	Germany	2.57	India	2.06
7	Venezuela	87.0	Mexico	3.19	Brazil	2.52	France	1.92
8	Russia	60.0	UAE	3.05	Saudi Arabia	2.38	Spain	1.53
9	Libya	41.5	Kuwait	2.74	Canada	2.26	Italy	1.48
10	Nigeria	36.2	Venezuela	2.64	S Korea	2.17	Taiwan	0.95
11	Kazakhstan	30.0	Norway	2.47	Mexico	2.13	Singapore	0.89
12	USA	21.3	Brazil	2.40	France	1.99	Netherlands	0.89
13	China	16.0	Iraq	2.39	Iran	1.76	Turkey	0.63
14	Qatar	15.2	Algeria	2.18	UK	1.71	Belgium	0.63
15	Algeria	12.2	Nigeria	2.17	Italy	1.64	Thailand	0.58
16	Brazil	12.2	Libya	1.88	Spain	1.56		
17	Mexico	11.7	UK	1.58	Indonesia	1.16		
18	Angola	9.0						
21	India	5.6	Indonesia	1.05	Thailand	0.94	Brazil	0.12
25	Indonesia	4.4	India	0.88	Turkey	0.68	Indonesia	0.11

Can USA drill its way out?

- US drilling cost $220 B in 2007 (API)
- 139 M bbl net added to US Reserves in 2008
- Annual US consumption: >7 B bbl
- On-shore areas may contain an additional 48.5 B bbl (6.4 years)
- Drilling allowed in most of Gulf of Mexico
- Deepwater Gulf of Mexico: 40.9 B bbl unproven (5.4 years)
  - Subject to hurricane disruption
- Off-shore areas unavailable in 2008 for drilling may contain 18.2 B bbl (2.4 years)

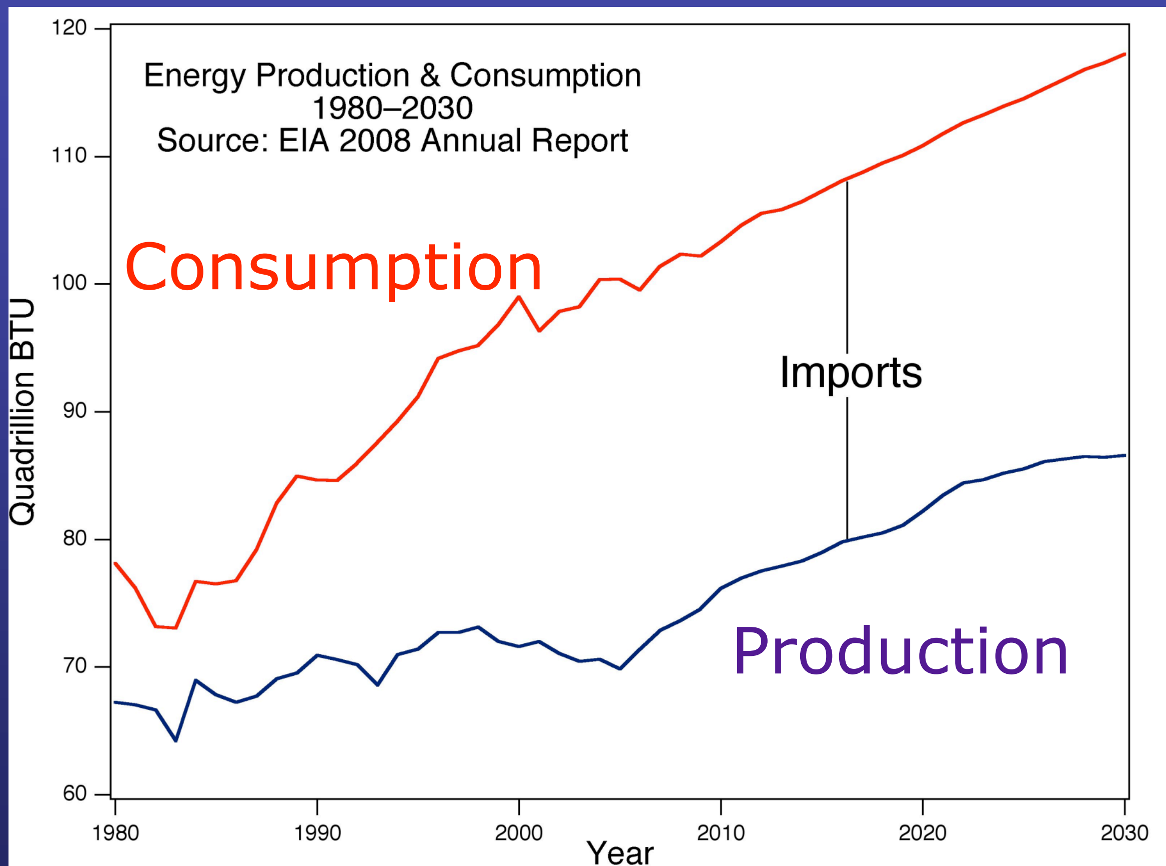
Source: EIA

Total Mean Oil Resources
(Undiscovered Technically Recoverable Resources)



USGS
science for a changing world

Domestic Energy Production Insufficient



Energy Information Administration
http://www.eia.doe.gov/

We will never run out of oil

- So what?
- More importantly: We will run out of **cheap** oil
- No previous change in primary energy source due to exhaustion of resources
  - Coal replaced wood as primary energy source in 1800's but more wood is burned now than ever before
- Each change (wood $\Rightarrow$ coal $\Rightarrow$ oil) has been the source of great opportunity

Keeping up with Future Demand

- 18.5 TW world demand, 3.4 TW used by US (2006)
- Only fusion and solar can possibly deliver 10+ TW annually. Solar: 600 TW annually practical
- World energy demand ~30 TW by 2050
- Need more even distribution of energy sources to diminish conflict
- Need to develop alternatives to petroleum

International Energy Agency: www.iea.org

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Fusion Power

- International Thermonuclear Experimental Reactor (www.iter.org)
  - $8–16 billion multinational project
    - US, EU, Japan, Russia, China, India, S Korea
  - 2009 building begins in France
  - 2018 fusion experiments begin
  - 2050 500 MW working reactor
- Was, is and always will be the power source of the future?

Solar Power

- Direct conversion to electricity
  - Photovoltaics
- Solar thermal electrical generation
  - Steam driven turbines
  - Storage as thermal energy
- Solar fuels
  - Hydrogen
  - Artificial photosynthesis (CH_4, EtOH…)
  - Biofuels

Harnessing Solar requires

- Understanding photodynamics
- Understanding charge transfer
- Carrier recombination and relaxation
- Photochemistry
- Photoelectrochemistry
- Formation of nanocrystalline semiconductors

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Solar Land Area Requirements

- U.S. Land Area: 9.1×10^{12} m^2 (incl. Alaska)
- Average Insolation: 200 W/m^2
- 2000 U.S. Primary Power Consumption: 99 Quads=3.3 TW
- 1999 U.S. Electricity Consumption = 0.4 TW
- Hence:
  3.3×10^{12} W/(2×10^2 W/m^2 x 10% Efficiency) = 1.6×10^{11} m^2
  Requires 1.6×10^{11} m^2/ 9.1×10^{12} m^2 = 1.7% of Land

Nathan S Lewis, Caltech, http://nsl.caltech.edu

Solar Land Area Requirements

Nathan S Lewis, Caltech, http://nsl.caltech.edu

Materials Issues

Materials used in solar energy conversion should be widely available and inexpensive

Material	Price / \$ kg^{-1}	World Production / kMt	World Reserves / kMt	R/P
As	2.09	59.2	1 776	30
Al	2.64	33 100	At 8%, 3rd most abundant element in Earth's crust	∞
Au	21 472	2.5	90	36
Cd	2.80	20.9	1 600	77
Cu	6.80	15 300	940 000	61
Ga	500 ~2000 as GaAs wafer	0.16	1 000	6250
Ge	880	0.1	no estimate	–
In	855	0.48	6	12.5
Sb	4.95	131	3 900	30
Se	66	1.39	170	122
Si	0.77 metallurgical grade 100-300 as wafer	4 700	At, 28%, 2nd most abundant element in Earth's crust	∞
Sn	11.44	273	11 000	40
Te	220	~0.128	47	367
TiO_2 (rutile)	4.65 / Mt 2.57 pigment grade	444	100 000	225
Zn	3.19	10 000	460 000	46

Can Humans Impact the Environment Globally?

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American Chemical Society Policy Statement

Careful and **comprehensive scientific assessments have clearly demonstrated that the Earth's climate system is changing rapidly** in response to growing atmospheric burdens of greenhouse gases and absorbing aerosol particles (IPCC, 2007). **There is very little room for doubt that observed climate trends are due to human activities**. The threats are serious and action is urgently needed to mitigate the risks of climate change. The reality of global warming, its current serious and potentially disastrous impacts on Earth system properties, and the key role emissions from human activities play in driving **these phenomena have been recognized by** earlier versions of this **ACS** policy statement (ACS, 2004), by other major scientific societies, including the **American Geophysical Union** (AGU, 2003), the **American Meteorological Society** (AMS, 2007) and the **American Association for the Advancement of Science** (AAAS, 2007), and by the **U. S. National Academies** and ten other leading national academies of science (NA, 2005).

Global Human Impact

- There is **no uncertainty** that human activity can effect the global environment
  - Fixed nitrogen (NH_3)
  - Ozone hole and CFCs
  - Lead (Pb)
  - Carbon Dioxide (CO_2)
  - Nuclear Winter
- Only discussion is on the **level of impact**: moderate to catastrophic
- The level of impact will depend on human **decisions & actions**

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Fixed Nitrogen
$N_2 + 3\ H_2 \rightarrow 2NH_3$

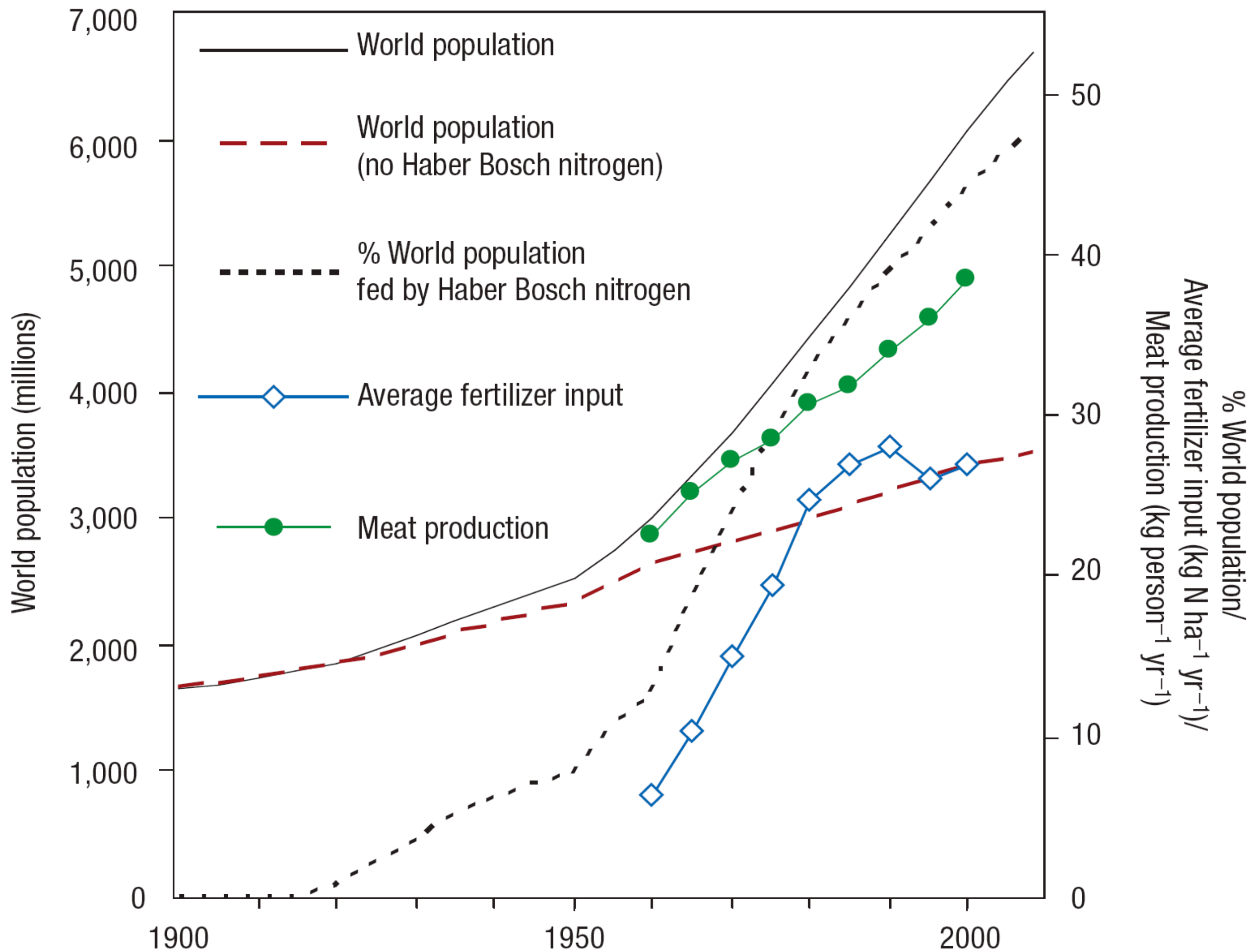
- Haber-Bosch Process: the world’s most important chemical reaction
- Animals need protein (a nitrogen containing molecule)
- Most plants lousy at incorporating nitrogen (need fertilizer)
- Humans now fix more nitrogen than all natural sources combined

1965

World population surpasses 3.3 billion

- Modern agriculture dependent on ammonia based fertilizer
- This cannot be replaced by dung
- If ammonia production were shut down, **3.2 billion people** could not be supported by agriculture
- NH_3 requires fossil fuels both for H_2 and for the energy to run the chemical reaction

NH_3 Synthesis is, arguably, the single most important industrial chemical reaction



Erisman, Sutton, Galloway, Klimont, & Winiwarter, Nature Geoscience 1 (2008) 636

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Mean Climate vs Weather

- Climate is easy to predict
  - 90% trivial to calculate
- But weather is what influences civilization
  - Final 10% crucial
- Greenhouse effect is essential to life
- Questions pertain to change

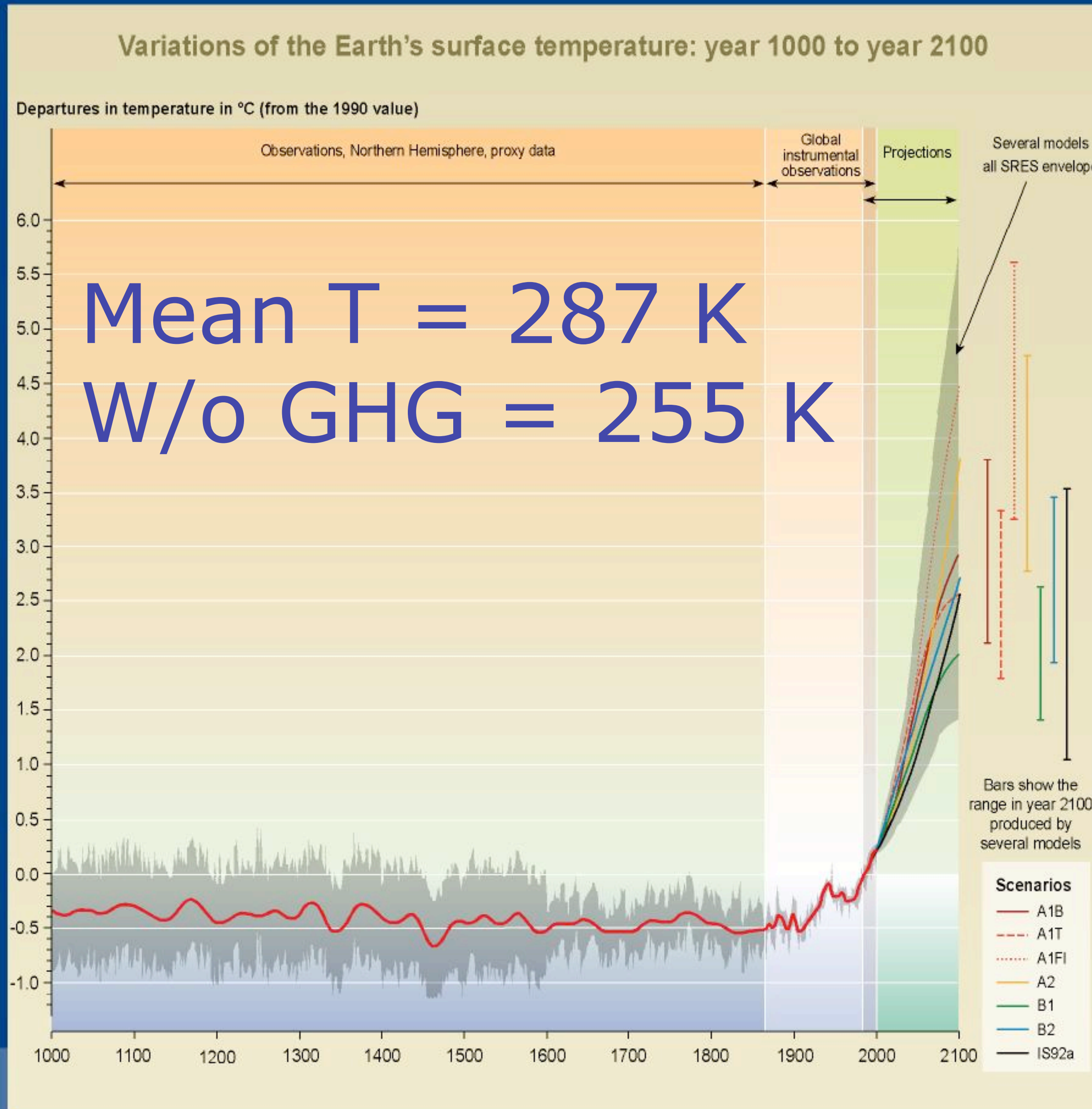
$$T_E = T_S \left(\frac{r_S}{2a_0} \right)^{1/2}$$

Blackbody radiation calculation of Earth's temperature

T_E = 279 K

Albedo ~30% $\Rightarrow$ 255 K

GHG $\Rightarrow$ 287 K



Mean T = 287 K

W/o GHG = 255 K

SYR - FIGURE 9-1b

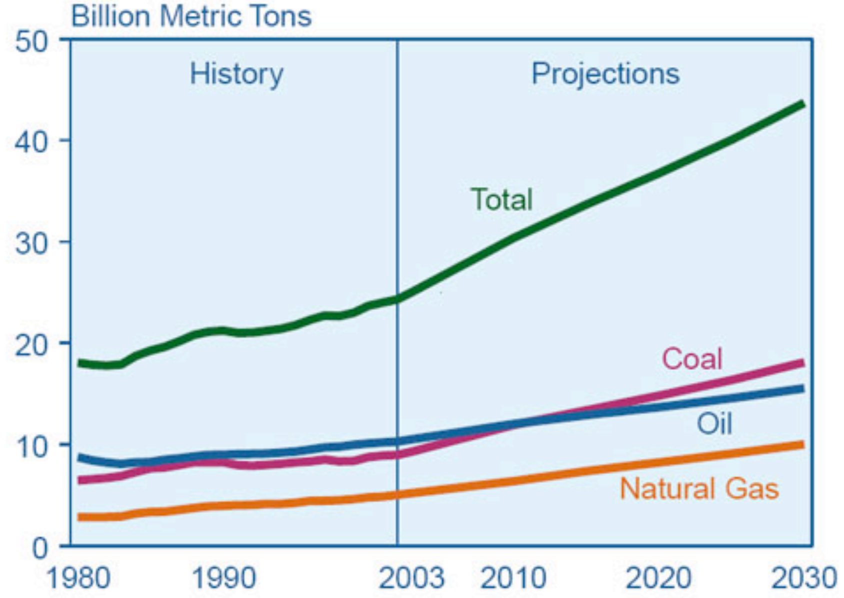
WMO UNEP

IPCC

INTERGOVERNMENTAL PANEL ON CLIMATE CHANGE

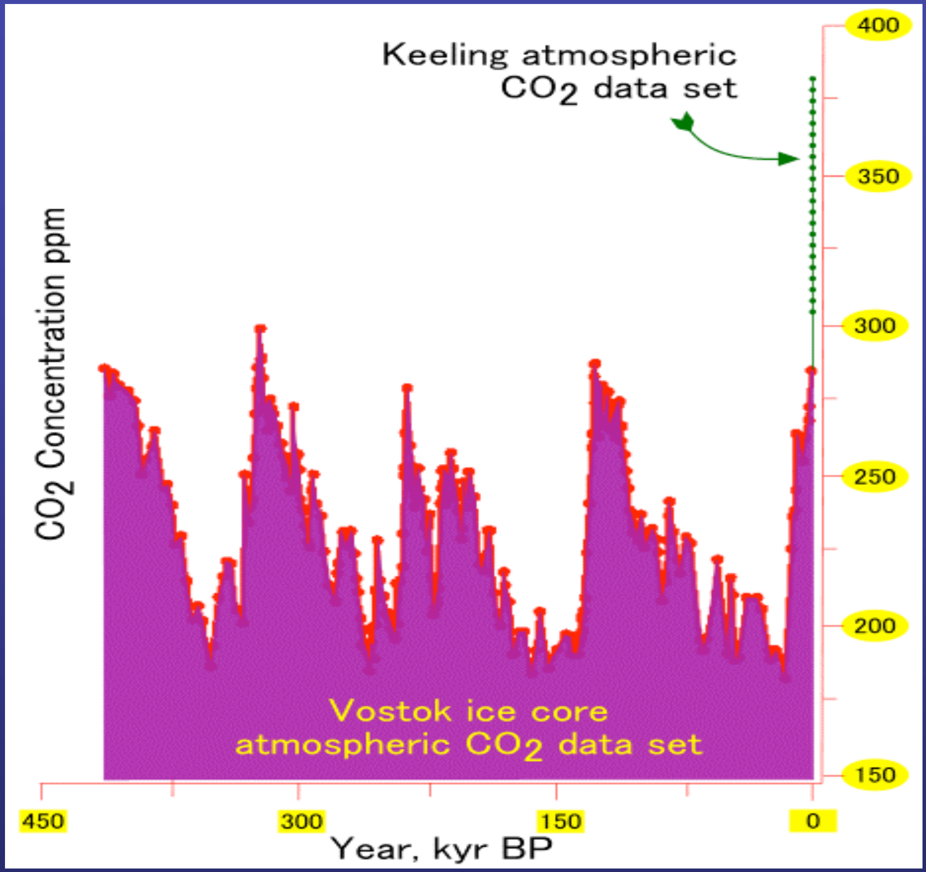
Increased CO_2 level due to Human Activity

Figure 66. World Carbon Dioxide Emissions by Fuel Type, 1980-2030



Sources: **History:** Energy Information Administration (EIA), *International Energy Annual 2003* (May-July 2005), web site www.eia.doe.gov/iea/. **Projections:** EIA, System for the Analysis of Global Energy Markets (2006).

Do you want to do this Experiment?



- Projected to reach 500 ppm by 2050
- 380 ppmv highest level in 10 million years
- Miocene: no Greenland ice sheet

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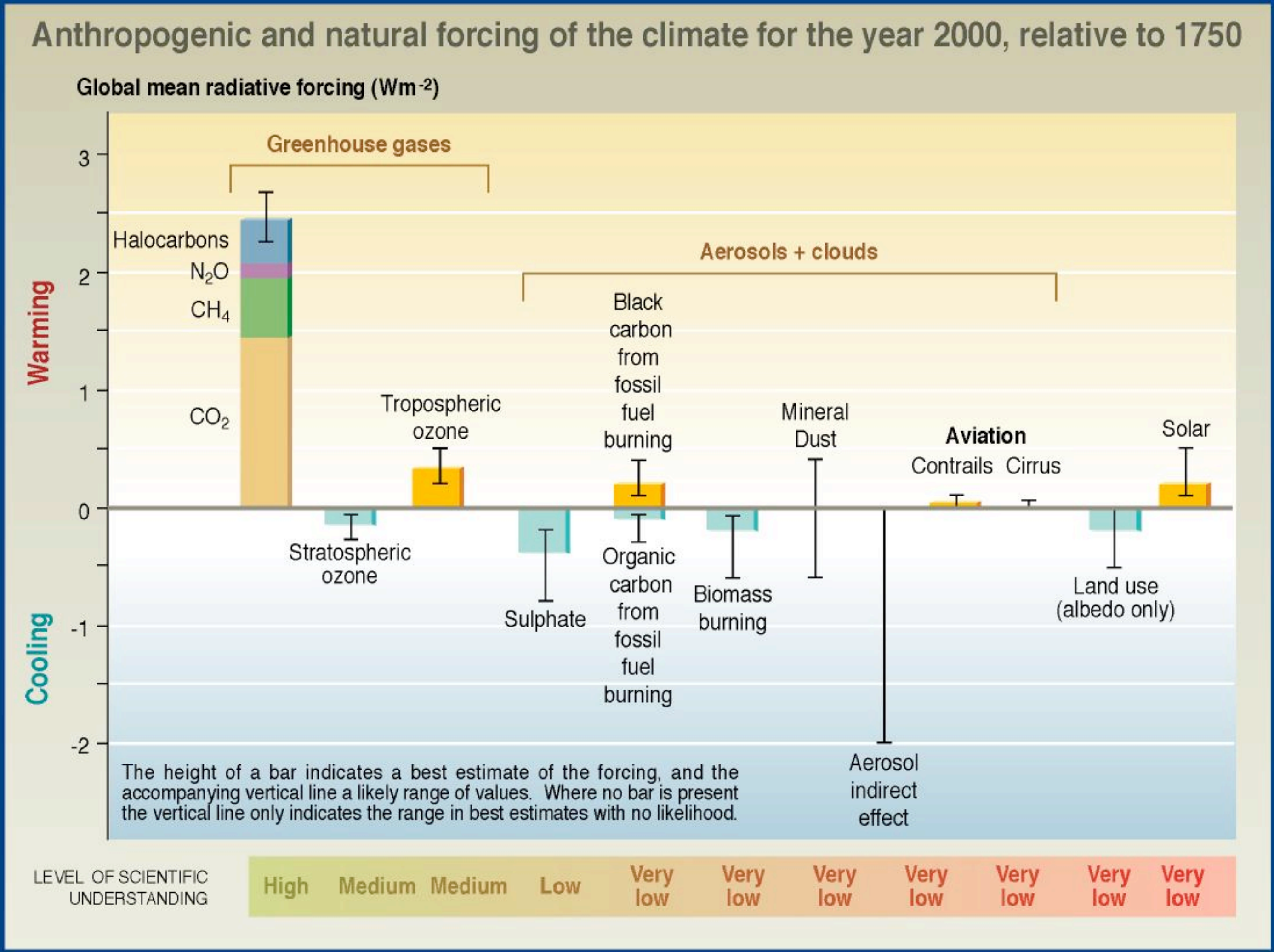
What is the role of chemistry/geochemistry?



SYR - FIGURE 2-2

IPCC | INTERGOVERNMENTAL PANEL ON CLIMATE CHANGE

WMO UNEP

What's the Difference between H_2O & CO_2?

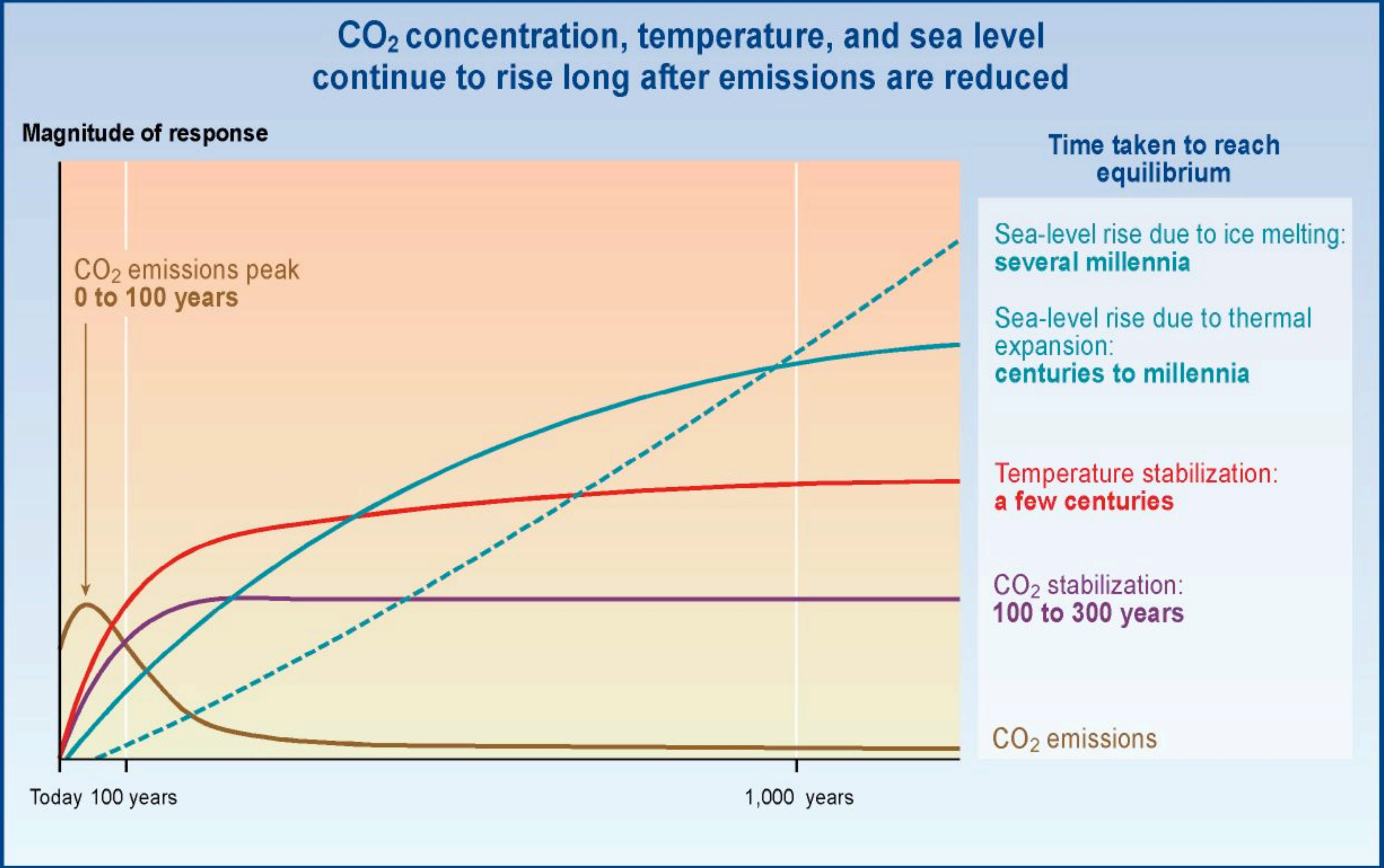
- The world 3/4 covered with an ocean of water not dry ice
- Vapor/liquid equilibrium (it rains)
- The greenhouse effect (~30°) of H_2O is saturated
- CO_2 absorbs IR at different frequency
- The oceans are a sink for CO_2 (1–2 Pg per year)
- Carbon removed by plants, precipitation, burial, photochemistry

Not all sources of CO_2 are the same

- Why doesn’t breathing make a difference?
- Why is burning wood from a managed forest different than burning oil, gas or coal?

Atmospheric Kinetics

- Chemical kinetics introduces time constants
- CO_2 atmospheric lifetime ≈ 50–200 years
- Global climate is a system in quasi-steady state (a massive coupled differential equation)

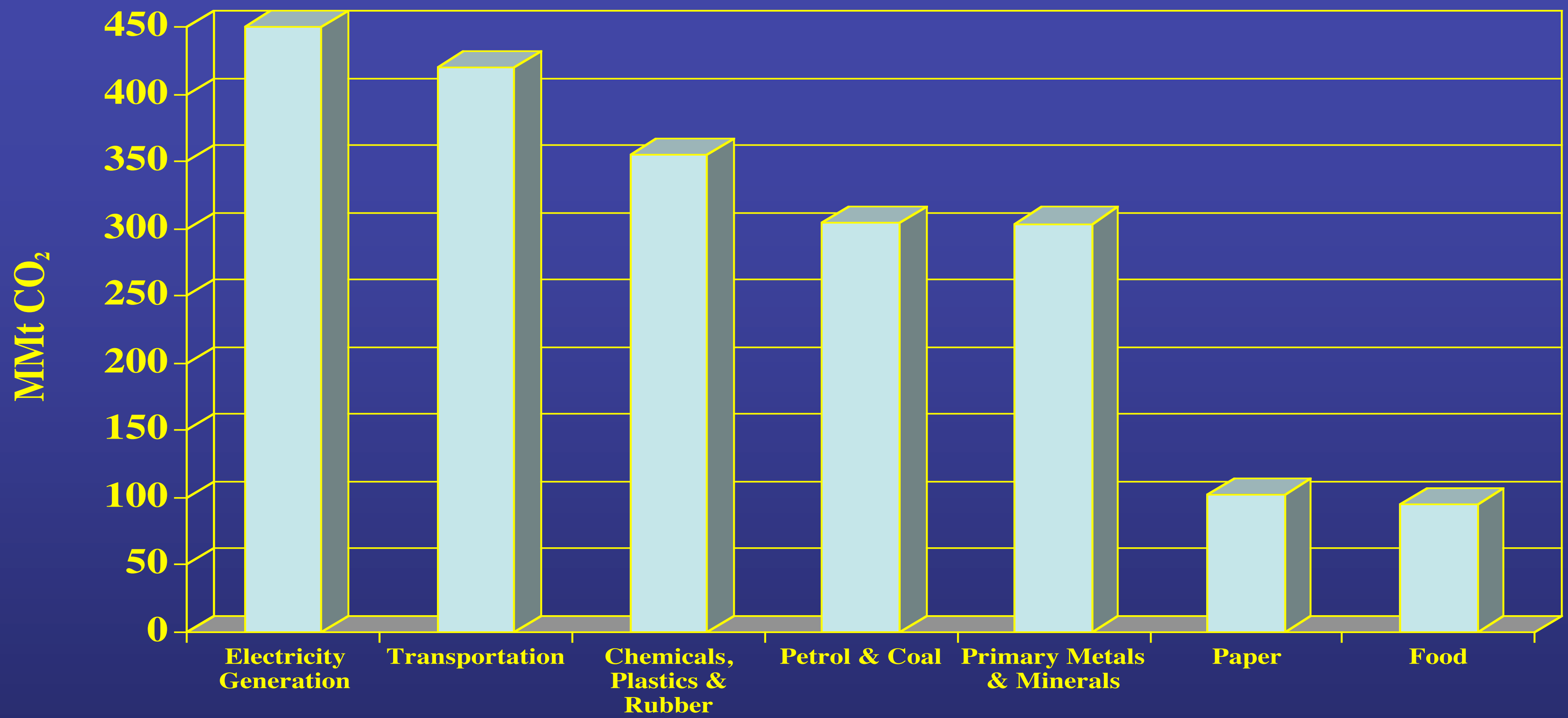


SYR - FIGURE 5-2

IPCC | INTERGOVERNMENTAL PANEL ON CLIMATE CHANGE

WMO UNEP

Carbon Emissions by Sector



Greater efficiency in the transportation, electricity & chemical sectors will have the greatest impacts in reducing emissions

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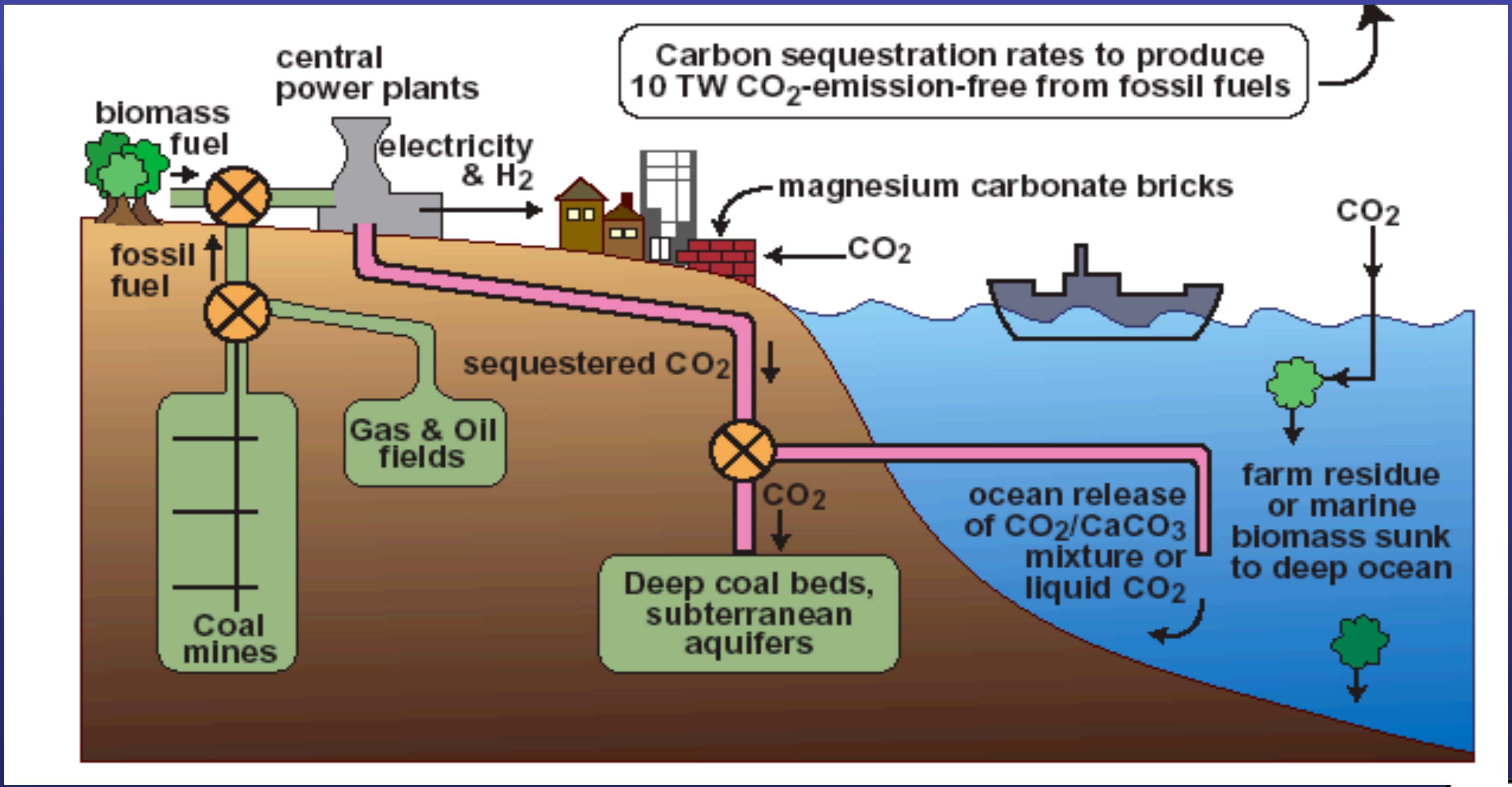
CO_2 Sequestration



Nathan S Lewis, Caltech, http://nsl.caltech.edu

DOE Sequestration Effort: Is it sufficient?

- $149 M budget (FY2009)
- Separations
- Geological Sequestration
  - Enhanced oil recovery, Coal seam methane, Deep saline reservoirs
- Mineralization
  - $MgCO_3$, CO_2 clathrates
- Photosynthetic routes
- Microbial methane or acetate production

DOE FY2009 Request (M$)

• Efficiency & Renewables	1,255	–27%
• Electricity Deliv & Relia	134	–3.3%
• Fossil Energy	1,127	+25%
• Nuclear Energy	1,419	+37%
• Total for Energy	3,936	+3.6%

Efficiency & Renewables FY2009 Request (M$)

• Hydrogen	146	−65%
• Biomass	225	+27%
• Solar	156	−12%
• Wind	53	+6%
• Geothermal	30	+51%
• Water	3	−70%
• Vehicles	221	+4%
• Buildings	124	+14%
• Industry	62	−4%
• Weatherization	59	−79%

Energy Efficiency

- Improved building, process, generation & transmission efficiency decreases energy intensity (intensity = $ GDP / J)
- Improved device efficiency is economically beneficial but does not automatically reduce consumption
  - better fuel mileage = more driving
  - more efficient air conditioning is used more
  - 1980–2000 US energy intensity –34%, use +26%
- Consumers tend to use as much energy as they can afford so efficiency gains don't always have full impact
- Industry can substantially reduce its energy use and intensity through efficiency gains & achieve better economics

Future Sources

- Multiple sources
- H_2 (methanol, formic acid)
  - Combustion and fuel cells
- Coal, methane, H_2O as H_2 sources
- Solar, wind, waves, geothermal
- What role for nuclear?
- Decoupling chemical industry from foreign controlled feedstocks
  - Syngas ($CO+H_2$) & bio/ag as feedstocks

Nuclear Power

- Important bridge technology
- Low CO_2 emissions
- 4.7 MMt of U_3O_8 @ \$130 kg^{-1}
- 85 year supply at current level
- 2500 year supply if fast breeders can be developed
  - Source: IAEA: www.iaea.org

The promise of nuclear may seem great but…

- Only 17% of nuclear fuel provided domestically (compared to 40% for oil)
- 2005 price (\$31.59 kg^{-1}) up by a factor of 5 since 2001
- Only 370 GWe installed worldwide
- Scaling to 12 TWe only 2.6 year supply of U @ \$130 kg^{-1}, only 77 for breeders
- No economical breeder cycle has been demonstrated (projected: 2015–2025)
- No solution to nuclear waste disposal has been decided upon

Technology Landscape

- Transportation Fuels
  - H_2, C1-4 alcohols, formic acid
  - Photovoltaics, fuel cells, batteries
- Electricity Generation
  - Photovoltaics, Wind, Waves
  - Nuclear?
  - Efficient generation and transmission
    - IGCC, superconductors, nanotube cables
  - Distributed networks, power electronics
- Feedstocks
  - Microbe/enzymatic digestion
  - Syngas, cellulose, (non-food) crops as chemical feedstocks

Leveraging Agriculture: Integrated Biorefinery

- 100 billion tons of plant tissue die each year = 10 times the mass of fossil fuel used
- Not efficient to grow plants for energy (energy density too low), ethanol displaces little oil, biodiesel good but cannot supplant all imports for fuel
- Use of cellulose & animal waste/byproducts could provide new feedstock for chemistry
- Technical challenges but low in GHG, renewable, enhances agricultural economics

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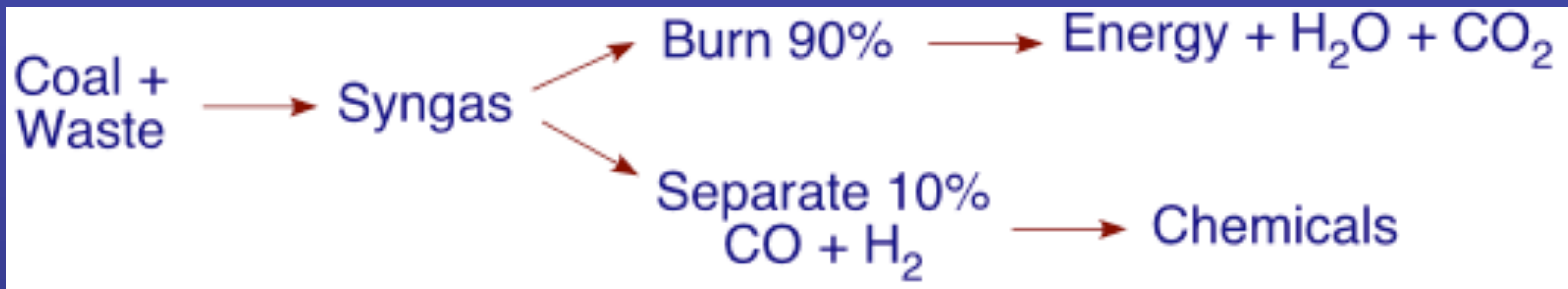
Challenges in Thermodynamics

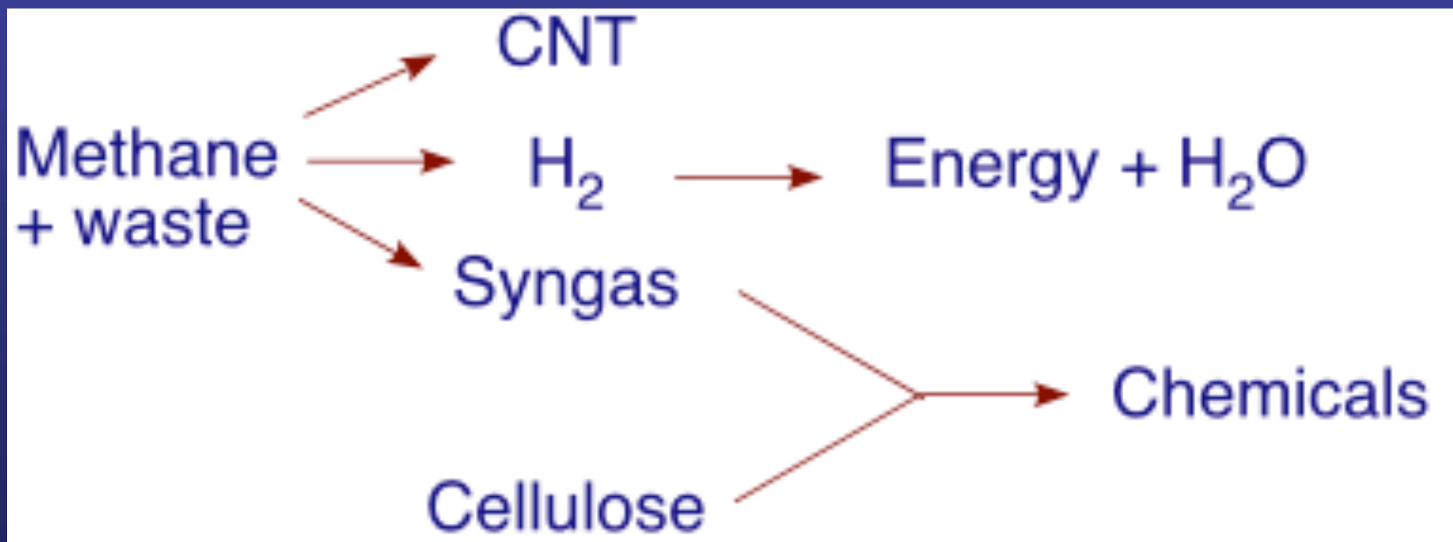
- What is the best cycle to produce H_2 from H_2O?
  - What can do better than carbothermal reduction?
  - Water electrolysis
  - $CaBr_2$/Fe oxide; H_2SO_4/HI; Cu–I cycles
- What is the best thermal cycle to produce carbon solids/liquids from CO_2?
  - Reactions with soils/clays
  - Reactions with minerals
  - Reactions with saline solutions
  - (Photo)Electro-chemical reduction to methanol

Challenges in Nanoscience & Solid State Chemistry

- Solar! Solar!! Solar!!!
  - Nanocrystalline materials for light conversions
  - Charge transfer dynamics
  - Thin films of conducting organic polymers
  - Solar fuels
- Hydrogen production
- Hydrogen storage
- Fuel cells
- Interfaces
  - Catalysis
  - Electrode/Electrolyte
- Materials
  - Superconductors
  - Thermoelectrics
  - Smart windows

Large-scale Catalytic Challenges





CO/CO_2 reactions, CNT production, GTL & other chemical transformations

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Managing Opportunities

- Systems approach
- Chemistry has an ESSENTIAL role to play in finding solutions
- The best science can only be implemented with good policy
- Pick a problem that interests you and work for solutions
- Sustainability as core of industrial, political and educational agenda