

15), but is much longer than values found in previous picosecond studies. This measurement of τ should at some time in the future be performed at intensities below 10^{13} photon/cm². This is at present beyond the capabilities of our apparatus.

As previous picosecond studies involved excitation intensities exceeding 10^{14} photon/cm² [for example, Beddard *et al.* (9, 25) used $I > 10^{15}$ photon/cm² and Yu *et al.* (4) and Seibert and Alfano (3) used $I > 6 \times 10^{14}$ photon/cm²], the data obtained must also reflect exciton annihilative processes. We believe the observations in (2–9) can be explained by their use of full mode-locked pulse trains and by a singlet-triplet annihilation process. Triplets, which evolve from singlets by intersystem crossing, live longer [$\tau_T = 30$ nsec in vivo (26)] than the time interval between pulses in the train [$\Delta t = 6.7$ nsec (9)]. Thus, the triplet population will increase from pulse to pulse until a steady-state value, N_{TSS} , is established. This value is limited at high intensities through a combination of singlet-singlet and singlet-triplet annihilation processes, eventually becoming independent of I . In this “saturated” regime, an appropriate Stern-Volmer equation for n_s is simply expressed as $dn_s/dt = -\gamma_{ST}N_{TSS}n_s$ and has a nearly exponential decay rate, $\gamma_{ST}N_{TSS}$, independent of I . This picture is similar to the observations in (5, 6, 9). The singlet state decay constant, $\gamma_{ST}N_{TSS}$, is observed to be in the range 10^{10} to 3×10^{10} sec⁻¹. Certainly these annihilation processes must occur at these intensities, and we suggest this as an alternative interpretation to the previous experimental observations.

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Effect of Infrared Transparency on the Heat Transfer Through Windows: A Clarification of the Greenhouse Effect

Abstract. *The various radiative, convective, and conductive components of the net heat transfer are calculated and illustrated for various infrared transparencies of covers such as would be used in architectural, greenhouse, or solar collector windows. It is shown that in the limiting cases of infrared opacity and infrared transparency the relative contributions of the three modes of heat transfer are altered, but all contribute significantly. The radiation shielding arguments pertain to the analogous greenhouse effect in the atmosphere.*

A number of letters have recently appeared dealing with the interpretation of the greenhouse effect (1, 2) and the etymology of the term (3). Fleagle and Businger (1) and Schwiesow (2) state that the infrared (IR) absorption by glass of the room temperature thermal radiation spectrum does little to alter the heat transfer characteristics of terrestrial greenhouses, and hence the thermal losses are essentially all due to convection. These authors cite the early work of R. W. Wood (1909), who “found that two model greenhouses, one covered with glass and the other with rock salt (which is transparent to both short- and long-wavelength radiation) reached very nearly the same high temperature” (1). They conclude that the greenhouse effect is due to the suppression of vertical convection by a rigid lid. The implication is that radiative transfer plays a minor role in the terrestrial greenhouse effect.

Indeed, a misconception exists because radiative transfer from the interior of a room, or from a nonevacuated flat plate solar collector to the covering glass window, is at least as important as convective transfer. The physical phenomenon involved, which explains Wood’s original observations, is that the sum of the convective and radiative losses is not changed appreciably by going from an IR-opaque cover (glass) to an IR-transparent cover (rock salt or polyethylene). However, the mix of the two contributions on the interior and exterior surfaces of the window is changed. This is

illustrated in Fig. 1 for the cases of vertical windows and horizontal skylights. These two cases differ by the nature of the free convective heat transfer coefficient at the interior surface of the window, and also by the effective sky temperature (4–6) as seen by windows in different orientations. The convection at the external surface is dominated by forced convection due to wind. The external convective heat transfer coefficient is the same for both orientations. For the example illustrated in Fig. 1, we have chosen the interior temperature as 21°C, the exterior temperature as 0°C, and the wind velocity as 5.36 m/sec. The effective sky radiation transfer temperatures, which depend on atmospheric conditions, are taken as –4.2° and –12°C below the ambient temperature for the vertical and horizontal surfaces, respectively. All units for heat transfer are watts per square meter.

Table 1 shows the mix of the different contributions to the heat transfer for different effective sky radiation temperatures. The sky temperature groupings are –11.4°, –4°C; –4.2°, –12°C; and –7°, –20°C for the vertical and horizontal windows, respectively, under different atmospheric conditions (4) for an exterior ambient temperature of 0°C. Figure 1 represents one of the examples in Table 1. The calculational methods used to arrive at these results are outlined at the end of the text.

In the results, the IR-opaque glass windows have higher temperatures than IR-

transparent covers because they absorb the thermal IR. Therefore, as the forced convective loss is proportional to the temperature gradient between the ambient and the external "glass" temperature, the external forced convection will be greater for the IR-opaque case than the IR-transparent case.

In conclusion, there certainly is an effect on the nature of the heat transfer associated with the IR opacity or transparency of a thermal insulating window. However, this effect is more in the component mix of the different transport mechanisms than in the net thermal transport. Moreover, radiative transport through windows is at least as important as convective transport. The IR-opaque glass acts as a radiation shield and reduces the radiative component of the heat

transfer to the exterior. For windows, this reduction in external radiative transfer is compensated to a large extent by an increase in the external forced convective transfer due to an increase in glass temperature caused by IR absorption from the interior.

A few comments are in order regarding the analogous greenhouse effect in the atmosphere. If the atmosphere did not contain any IR-absorbing components (primarily dust, water vapor, and carbon dioxide), the effective nighttime sky radiation temperature would approach that of a 3°K blackbody. Then radiative cooling of the earth would be substantial, comparable to that experienced on the moon. The atmospheric blanket provides a radiation shield, which is in principle the same as the glass window.

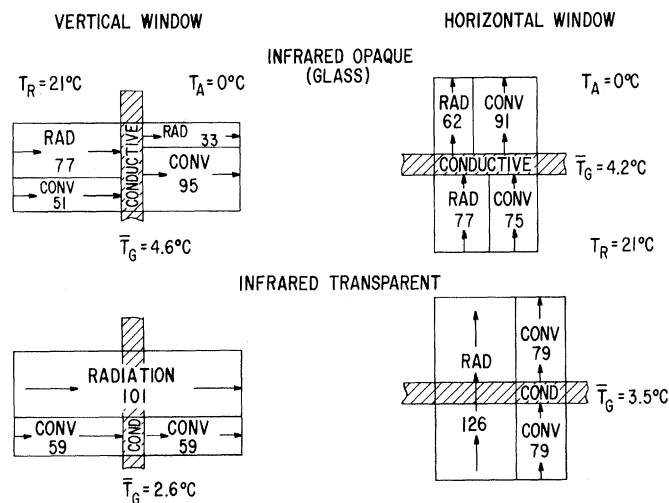


Fig. 1. Mix of radiative, convective, and conductive transport through horizontal and vertical windows. The thermal flux is in watts per square meter.

Table 1. Breakdown of the various contributions to the thermal flux through the window for different sky temperatures representative of different weather conditions. The interior and exterior glass surface temperatures are T_{G-} and T_{G+} , respectively. The various heat transfer components are $Q_{RG,R}$, room to glass, radiative; $Q_{RG,C}$, room to glass, convective; $Q_{GA,R}$, glass to ambient, radiative; $Q_{GA,C}$, glass to ambient, convective; $Q_{RA,R}$, room to ambient, radiative; Q_{total} , net heat transfer (sum of radiative and convective); and $U = Q_{total}/(T_R - T_A)$, where T_R is the room temperature and T_A the ambient temperature. Results are based on $T_R = 21^\circ\text{C}$, $T_A = 0^\circ\text{C}$, and wind velocity = 5.36 m/sec.

Window	Temperature (°C)			Heat transfer component (watt/m ²)						U (watt m ⁻² °K ⁻¹)
	T_{sky}	$T_{\text{G-}}$	$T_{\text{G+}}$	$Q_{\text{RG,R}}$	$Q_{\text{RG,C}}$	$Q_{\text{GA,R}}$	$Q_{\text{GA,C}}$	$Q_{\text{RA,R}}$	Q_{total}	
<i>IR-opaque, ordinary glass</i>										
Vertical	-1.4	4.9	4.3	75	50	24	102	0	126	6.00
	-4.2	4.5	4.0	77	51	33	95	0	128	6.10
	-7.0	4.3	3.7	78	53	43	88	0	131	6.23
Horizontal	-4.0	5.2	4.6	74	70	35	108	0	144	6.86
	-12.0	4.5	3.9	77	75	62	91	0	153	7.26
	-20.0	3.8	3.1	80	79	86	73	0	159	7.58
<i>IR-transparent</i>										
Vertical	-1.4	2.8	2.5	0	59	0	59	90	149	7.10
	-4.2	2.8	2.5	0	59	0	59	101	160	7.62
	-7.0	2.8	2.5	0	59	0	59	110	169	8.05
Horizontal	-4.0	3.7	3.4	0	79	0	79	100	179	8.52
	-12.0	3.7	3.4	0	79	0	79	126	205	9.76
	-20.0	3.7	3.4	0	79	0	79	150	229	10.9

The details are different as the atmosphere is diffuse rather than concentrated, and convective mixing occurs within the atmosphere rather than at a fixed outer boundary.

Calculational methods. The heat transfer results in Table 1 were obtained as follows. The heat transfer was broken down into components:

1) The convective heat transfer per unit area from the room interior to the inner glass surface is $Q_{RG,C}$. In winter, the transport parameters and temperature gradients are large enough that the turbulent free convective heat transfer coefficients are the appropriate choice. For a boundary layer temperature of $\approx 10^\circ\text{C}$, these relations are given by (7, 8)

$$Q_{RG,C} \approx \begin{cases} 1.23(\Delta T_{RG-})^{4/3} \text{ vertical} \\ 1.78(\Delta T_{RG-})^{4/3} \text{ horizontal} \end{cases} \quad (1)$$

where $\Delta T_{RG-} = T_R - T_{G-}$, where T_R and T_{G-} are the room and interior glass surface temperatures.

2) The radiative heat transfer from the room to the interior glass surface, $Q_{RG,R}$, given by

$$Q_{RG,R} = \sigma \epsilon_{G-} (T_R^4 - T_{G-}^4) \quad (2)$$

where ϵ_{G-} is the IR emittance (absorptance) of the glass, and σ is the Stefan-Boltzmann constant, 5.67×10^{-8} watt $\text{m}^{-2} \text{ } ^\circ\text{K}^{-4}$.

3) The thermal radiation heat transfer from the room interior to the ambient exterior, $Q_{RA,R}$, given by

$$Q_{RA,R} = \sigma \tau (T_R^4 - T_{sky}^4) \quad (3)$$

where T_{sky} is the effective sky radiation temperature (4), and τ is the IR transmittance of the window. For ordinary glass, which is opaque to IR, $\tau = 0$.

4) The conductive heat transfer through the glass of thickness d and thermal conductivity k_{glass} , $Q_{G-G+,C}$

$$Q_{G-G+,C} = (k_{glass}/d) \Delta T_{G-G+} \quad (4)$$

For glass, $k_{glass} \approx 0.78$ watt $\text{m}^{-1} \text{ } ^\circ\text{K}^{-1}$. At a thickness of 0.32 cm, $k/d \approx 250$ watt $\text{m}^{-2} \text{ } ^\circ\text{K}^{-1}$.

5) The forced convective heat transfer at the exterior surface, $Q_{G+A,C}$. For turbulent flow, which is appropriate in this case,

$$Q_{G+A,C} \approx 6.13 V^{0.8} \Delta T_{G+A} = 23.5 \Delta T_{G+A} \text{ watt } \text{m}^{-2} \quad (5)$$

for a wind velocity V of 5.36 m/sec; T_A is the ambient temperature.

6) The radiant heat transfer between the exterior glass surface and the ambient exterior, $Q_{G+A,R}$

$$Q_{G+A,R} = \sigma \epsilon_{G+} (T_{G+}^4 - T_{sky}^4) \quad (6)$$

The continuity of the net thermal current from the interior to the exterior gives

$$Q_{RG-,C} + Q_{RG-,R} + Q_{RA,R} = Q_{RA,R} + Q_{G-G+,C} = Q_{RA,R} + Q_{G+A,R} + Q_{G+A,C} \quad (7)$$

Equation 7 represents two simultaneous equations with two unknowns, T_{G-} and T_{G+} , which can be solved readily by iterative numerical techniques. In Eq. 7 we have added the $Q_{RA,R}$ contribution to all terms to illustrate continuity of the net energy transport. This term cancels out in the determination of the glass temperatures. In the text we specifically considered the two limiting cases of IR opacity (glass) and IR transparency (rock salt or polyethylene). Using the techniques sketched here, any results between these limits can be obtained readily. For the case of glass, which is opaque to room temperature thermal IR, $\epsilon_{G-} = \epsilon_{G+} = 0.88$. For the cases of IR-transparent materials, $\epsilon_{G-} = \epsilon_{G+} = 0$, while the IR transmittance is reduced from unity only by the dual-surface IR reflectivity. The single-surface thermal IR reflectance of glass is ≈ 0.12 . Assuming that the IR-transparent medium has the same single-surface reflectivity for a lambertian (diffuse) IR source as glass, the dual-surface transmittance is given in terms of the single-surface reflectivity r by the relation

$$\tau = (1-r)^2/(1-r^2) \approx 0.79 \quad (8)$$

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Total Synthesis Benzene and Its Derivatives as Major Gasoline Extenders

Abstract. Synthesized benzene and simple alkylated derivatives are proposed as nonpetrochemical gasoline components. Feasible raw materials include coal, coke, charcoal, and carbonaceous wastes. The basic synthesis consists of the formation of lithium carbide by reaction of the metal with carbon, hydrolysis of the carbide to acetylene, cyclization of acetylene to benzene, and regeneration of lithium metal. Total synthesis benzene is substantially different from other synthetic hydrocarbon fuels in that its hydrogen content is obtained from water so that hydrogen gas is not needed as a major reactant.

Total synthesis benzene (TSB) should be considered as a possible fuel for internal combustion engines. This proposal is an alternative to those approaches to coal liquefaction that involve deep or extensive hydrogenation, pyrolysis, and the generation of alcohols. These synthetic hydrocarbon methods depend upon hydrogen gas as a major reactant, whereas in the TSB method the hydrogen is obtained from a water reaction.

Benzene synthesis is the basis of a standard technique now employed in radiocarbon dating (1-3). A large variety of starting materials can be used, including charcoal, other chars, organic substances, carbonates, and carbon dioxide. Because of the limited size of these samples, extensive efforts have been made over the past years to optimize the synthesis efficiency, reliability, and ease of

operation. At the present time, 90+ percent yields are routinely obtained (4, 5).

To produce TSB in industrial quantities, a modified synthesis with recycled lithium is outlined in Table 1. The fused salt electrolyses of both alkali metal hydroxides (procedure 1) and chlorides (procedure 2) are established industrial procedures (6). The chloride procedure has the advantage of greater electrolysis efficiency and the production of a valuable by-product, chlorine gas. The hydroxide electrolysis route is simpler but consumes more electricity because of a side reaction of water with the metal. The alternative technique in which lithium oxide is reduced with carbon (procedure 3) can be carried out with most of the energy supplied by direct combustion. These methods regenerate the metal intermediate used in the production of acetylene.

Standard Gibbs free energy changes (ΔG°) for the formation of lithium carbide and for the reduction of lithium oxide with carbon are shown in Fig. 1. In the latter reaction, the carbon monoxide generated is expeditiously removed with a good vacuum system; lithium vapor is also produced. Extraction of these two gaseous products from the immediate reaction zone displaces the equilibrium and results in usable oxide reductions, despite the positive ΔG° values. Lithium vapor is condensed in the presence of feedstock carbon to form the carbide.

The introduction of pure carbon into the reactor by the decomposition of carbon monoxide feedstock is also a possible approach. This procedure eliminates the ash separation step. Carbon monoxide is continuously produced when carbon dioxide is passed over a heated char. An alternative would be to

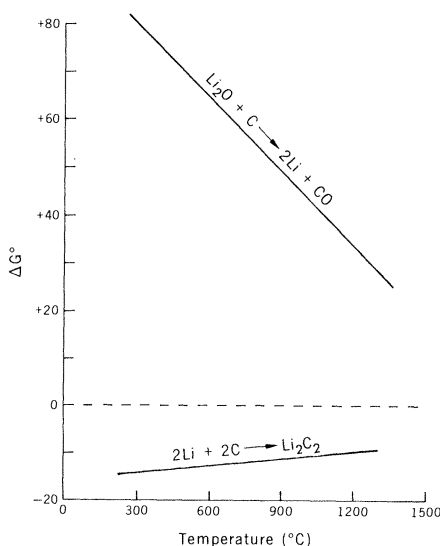


Fig. 1. Standard Gibbs free energies for the formation of lithium carbide and for the reduction of lithium oxide with carbon.