

Paper SNI 6/3

A LOCAL PROPAGATION THEORY FOR VAPOR EXPLOSIONS

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SUMMARY

Explosive boiling, defined as energy transfer leading to formation of vapor rapidly enough to produce large shock waves, has been widely studied in a number of contexts. Depending upon the nature and temperatures of the liquids and mode of contacting, large-scale mixing and explosive vaporization may occur, or alternatively, only relatively non-energetic, film-type boiling may exist. The key difference is whether a mechanism is operative for increasing the liquid-liquid interfacial area in a time scale consistent with the formation of a detonation wave. Small drops of a cold volatile liquid were dropped onto a free surface of a hot, non-volatile liquid. The critical Weber number for coalescence is obtained from the envelope of the film boiling region. Markedly different behavior for the two hot liquids is observed. A "splash" theory for local propagation of vapor explosions in spontaneously-nucleating liquid-liquid systems is now formulated. After a random contact is made, explosive growth and coalescence of the vapor bubbles occurs as soon as the surrounding pressure is relieved, resulting in a high-pressure vapor layer at the liquid-liquid contact area. This amounts to an impact pressure applied to the free surface, with a resulting velocity distribution obtained from potential flow theory. The peak pressure predictions are consistent with data for Freon-oil mixing, but further evaluation will await additional experimental data. Nevertheless, the current inference is that a UO_2 -Na vapor explosion in a reactor environment cannot be visualized.

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¹This work was supported by a grant from the Energy Research and Development Administration.

I. Introduction

Explosive boiling, defined as energy transfer leading to formation of vapor rapidly enough to produce large shock waves, has been widely studied in a number of contexts. One can distinguish the following classifications:

1) Liquid-liquid contact. Here a very hot liquid is mixed with a cold, volatile liquid. Depending on the nature and temperatures of the liquid, and mode of contacting, large-scale mixing and explosive vaporization may occur, or alternatively, only relatively non-energetic, film-type boiling may exist. The key difference is whether a mechanism is operative for increasing the liquid-liquid interfacial area in a time scale consistent with the formation of a detonation wave.

2) Liquid-solid contact. Even when no new heat transfer surface is produced by the energy transfer, Skripov, et al. have demonstrated that explosive boiling can be obtained by pulse-heating fine platinum wires immersed in various liquids.⁸ If the homogeneous nucleation temperature is reached within a minimum time, which depends on the liquid (and possibly also on the solid surface), nucleation due to pre-existing sites is suppressed, and pressure pulses are observed at surface temperatures in excellent agreement with homogeneous nucleation theory. We limit ourselves in this work to liquid-liquid interactions in which the principal mechanism for vapor production is spontaneous nucleation, which refers to nucleation due to local density fluctuations, and may be homogeneous or vapor-free heterogeneous in character.³

II. Liquid-Liquid Surface Impaction Experiments

Small drops of a cold volatile liquid were dropped onto a free surface of a hot, non-volatile liquid by Waldram¹, and the results have been interpreted by Fauske² and by Waldram, et al.³ The drops either rebounded smoothly, resulting in film (or Leidenfrost) boiling, or coalesced with the hot liquid depending upon whether the impact Weber number was less than or greater than some critical value. If coalescence occurred, the droplet would either evaporate smoothly or spatter explosively after some delay time, depending on whether the hot liquid temperature was below or above the homogeneous nucleation of the cold liquid. If the initial interface temperature, calculated from conduction theory, was above the homogeneous nucleation temperature, a fine spray of a few spattered droplets would form immediately, but the bulk droplet would usually remain in film boiling. The critical role of the mode and condition of liquid-liquid contacting was thus verified. Some additional experimental work has been carried out with Freon - 113 and pentane as the volatile fluids, and with Dow-Corning 710 Silicone oil and glycerol as the hot fluids, extending the ranges of diameters and temperatures for the critical Weber number for coalescence. Fig. 1 shows typical data for pentane drops on silicone oil, showing the same general trends as in previous work. The critical Weber number for coalescence is obtained from the envelope of the film boiling region, and is plotted in Fig. 2 for Freon-113 on silicone oil and glycerol. Markedly different behavior for the two hot liquids is observed. We_{cr} for silicone is higher at all temperatures than for glycerol by a factor of 2-4, increasing with temperature and with drop diameter. For

glycerol We_{cr} is nearly independent of both T_h and d ; moreover, spattering does not occur after wetting, but only isolated, fairly weak centers of vapor formation. Fig. 3 shows somewhat similar trends for pentane on silicone oil, although a much stronger dependence on temperature for $T_h \geq 200^\circ\text{C}$ is observed. This is accompanied by visible vapor streaming from the underside of the drop. For $T_h = 275^\circ\text{C}$ We_{cr} increased very markedly, and for the smaller drops could not be measured with the available release heights. It is believed that this difference in behavior of Freon - 113 ($T_{cr} = 214.1^\circ\text{C}$) and pentane ($T_{cr} = 196.5^\circ\text{C}$) is related to the fact that the interface temperature $T_i = T_{cr}$ for pentane-glycerol when $T_h = 256.5^\circ\text{C}$, but for pentane-silicone oil when $T_h = 307.9^\circ\text{C}$. The data were correlated by a least-squares routine (Figs. 4 and 5) by an equation of the form:

$$We_{cr} = A + B\eta^n ; \quad \eta = \frac{d}{\lambda} \left(\frac{T_i - T_{sat}}{T_{cr} - T_i} \right) \quad (1)$$

where A , B , and n are constants which depend upon the liquid-liquid combination (Table 1); T_{sat} and T_{cr} are the saturation and critical temperatures of the volatile liquid; $\lambda = 2\pi(\sigma/\rho_c g)^{\frac{1}{2}}$ is the capillary wavelength of the cold liquid; and T_i is the calculated initial interfacial temperature based on the conduction formula:

$$\frac{T_h - T_i}{T_i - T_c} = \sqrt{\frac{k_c \rho_c c_c}{k_h \rho_h c_h}} \equiv R \quad (2)$$

whence

$$T_i = \frac{T_h + RT_c}{R + 1} \quad (3)$$

Since $n > 0$, the form of the temperature dependence ensures that wetting is not possible at any drop height where the interfacial contact temperature is equal to the volatile liquid critical temperature, in accord with physical necessity. At low temperatures the second term becomes small, indicating that vaporization from the approaching droplet plays a minor role. The empirical constants are different for different liquid pairs, and depend upon physical properties and surface wetting effects. Thus, for silicone oil, $n = 0.25 - 0.75$ indicating a temperature dependence which is weak far from the critical point, but becomes dominant as the critical point is approached. Clearly, more information concerning the stability of the gas / vapor layer between dissimilar liquid surfaces at different temperatures, which depends both upon the surface evaporation rates and the long-range London forces, would be helpful.

III. Splash Theory for Vapor Explosions

We shall now formulate an unstable film-boiling model for vapor explosions in spontaneously-nucleating liquid-liquid systems. We begin with the assumption that locally a hot non-volatile liquid is separated from a cold volatile liquid by a film of vapor (and possibly gas). The vapor may have been produced by a previous contact between the two liquids; the gas may have been entrained in the mixing process, or may have been released from solution or adsorption. We assume that a random contact is made between the two liquids. This contact may be

due to capillary instability of the vapor film, in which the contact radius may be of the order of the capillary wavelength

$$\lambda_j = 2\pi \sqrt{\frac{\sigma_1}{g(\rho_{fj} - \rho_v)}} \quad (4)$$

where $j = 1$ for cold fluid, and $j = 2$ for hot fluid. In this case the appropriate mean vapor film thickness may be given by the modified Taylor stability analysis of Berenson for film boiling⁴:

$$b = 2.35 \left[\frac{\mu_v k_v (T_2 - T_{1s})}{h_{fg} \rho_v g (\rho_{f1} - \rho_v)} \sqrt{\frac{\sigma_1}{g(\rho_{f1} - \rho_v)}} \right]^{\frac{1}{2}} \quad (5)$$

As pointed out by Henry and Fauske⁵, homogeneous nucleation cannot occur until sufficient heat has been absorbed by the cold fluid to stabilize the existence of a bubble of critical radius, r_n , with liquid at the homogenous nucleation temperature T_n . This thermal-energy time is given approximately by:

$$t_n = \frac{r_n^2}{\alpha_1} \left(\frac{T_i - T_1}{T_i - T_n} \right)^2 \quad (6)$$

This time is typically $\sim 10^{-9}$ sec. Likewise, from the Rayleigh equation for inertia-dominated bubble growth, the time for an order-of-magnitude increase in radius, t_g is $\sim 10^{-9}$ sec. On the

other hand, the acoustic relief time is

$$t_a = \frac{2\ell}{c} \quad (7)$$

where ℓ is the mean distance to a free surface and c is the sonic velocity in the liquid. In the Henry-Fauske theory, $\ell = \xi d$, where $\xi < 1$ is a shape factor related to the degree of spreading of the drop on the hot liquid surface. In the present theory a tongue of liquid, rather than a drop, contacts the opposite surface, and the contact radius, a , is related to the Taylor instability wavelength, by

$$a = \gamma \lambda_j \quad j = 1, 2 \quad (8)$$

where γ is a random variable. From Eq. (7), since $a \sim \ell$ and $\lambda_1 \approx 0.5$ cm, $t_a \sim 10^{-5}$ sec $\gg t_h + t_g$. Thus, by the time the bubbles are able to grow through acoustic pressure relief, the thermal boundary layer has become at least an order-of-magnitude thicker than the minimum for nucleation. For Freon-22 at atmospheric pressure⁵, homogeneous nucleation theory predicts the spontaneous nucleation rate $J = 1.3 \times 10^6$ cm⁻³ sec⁻¹, ($r_n = 40$ Å) at $T_i = 54^\circ\text{C}$, and 4.2×10^{22} cm⁻³ sec⁻¹ ($r_n = 29$ Å) at $T_i = 60^\circ\text{C}$. At the latter temperature this would imply one critical-radius bubble for each surface element of area 10^{-14} cm² in the thermal boundary layer by the time, t_a , has elapsed. Clearly, therefore, an explosive growth and coalescence of the vapor bubbles occurs as soon as the surrounding pressure is relieved, resulting in a high-pressure vapor layer at the liquid-liquid contact area. This amounts to an impact pressure applied to the free surface over the region $r < a$, with a resulting velocity distribution obtained from

potential flow theory. The normal velocity of the surface for $r > a$ is given by⁶

$$v(y) = \beta (y^{-\frac{1}{2}} - \tan^{-1} y^{-\frac{1}{2}}) \quad (9)$$

where $y \equiv \frac{r^2}{a^2} - 1 > 0$ and $\beta = \frac{2U}{\pi}$. Here U is the impact velocity of a flat-nosed cylinder of radius a which produces the same total force impulse, I . In this case it is shown that

$$I = \frac{4}{3} \rho_f a U \quad (10)$$

for the impulse due to the vapor layer. It follows that

$$I \geq \pi a^2 t_a (p_n - p_\infty) \quad (11)$$

where p_n is the vapor pressure of the volatile liquid at the spontaneous nucleation temperature. To justify this reasoning, one can make simple order-of-magnitude calculations. A second acoustic pressure relief occurs through radial expansion of the free surface of the cylindrical tongue of liquid making contact with the hot liquid surface. During this acoustic relief period, an impact velocity is transmitted to both liquid surfaces, so that the lateral displacement of the adjacent surfaces of the vapor film is given by $2Ut_a$. Since the thickness of the heated zone is $2\sqrt{\alpha t_h}$, the ratio $N_1 = Ut_a / \sqrt{\alpha t_h}$ determines the time scale for radial expansion of the high-pressure vapor layer into the adjoining free vapor space. For $T_i = 60^\circ\text{C}$, $U \sim 400$ cm/sec

from eqs. (10) and (11); $t_a \sim 10^{-5}$ sec; $t_h \sim 10^{-9}$ sec; so that $N_1 \sim 10^3$. Hence the pressure falls quickly after the acoustic relief period. The pressure within the bubbly layer rises quickly during the heating and growth time ($t_h + t_g \sim 10^{-9}$ sec). Note that surface tension forces do not relax until significant bubble growth and coalescence occurs, but the time scale for the pressure increase is still very short compared to t_a . Eq.(11) implies that the lower bound for the impulse is obtained by neglecting the contributions during the pressure rise and fall times.

The data were taken only with $j=1$ (cold liquid drops impacting the bulk hot liquid), but it is assumed here that the correlation holds for $j=2$, also. This states that the relative normal velocity of the two liquids determines the minimum vapor film thickness between them, and hence the probability of coalescence. In any case it will be seen that the predicted pressure curves are not very different for $j = 1$ and 2. Unless otherwise stated, we employ $We = We_1$.

It is known that the probability distribution for the small-size range of fragmented material follows a log-normal distribution, and if we assume a similar distribution for γ , one obtains, from Eqs.(8) and (15)

$$P(\bar{We} > We_{cr}) = \frac{1}{\sqrt{\pi}} \int_{X_{cr}}^{\infty} e^{-t^2} dt \quad (16)$$

where

$$X = \frac{1}{5} \log \frac{\gamma}{\bar{\gamma}} \quad (17)$$

Here S and $\bar{\gamma}$ are the standard deviation and mean, and $X = X_{cr}$ when $We = We_{cr}$. The mean time for one successful propagation step is thus

$$t_m = \frac{t_h + t_a + t_g + t_s}{P(\bar{We} > We_{cr})} \quad (18)$$

where the splash time, t_s , given by

$$t_s = b/\bar{v} \sim 10^{-4} \text{ sec} \quad (19)$$

is the rate-limiting step at any one contact point. However, there will be a large number of random contacts on a macroscopic scale, and the maximum detected pressure, p_d , can be approximated by

$$p_d = \epsilon p_n; \quad \epsilon = m t_a / t_m \leq 1 \quad (20)$$

where m is the average number of pressurized contact areas at any instant. For $T_i \leq T_n$, $t_m = \infty$, so that no pressure wave is predicted. When T_i increases slightly above T_n , $\epsilon \sim 1$, since mutual pressurization ensures that the detected pressure can never exceed the maximum vapor pressure within the system. However, as T_i increases beyond this point, p_d begins to decrease, in view of Eq.(18), and eventually approaches zero at the critical temperature. Using the parameters for Eq.(1) from Fig. 4, Figs. 6-8 show a comparison of the predictions of Eqs. (16)-(19) with data^{5,7} in which Freon-12 and Freon-22 were contacted with mineral oil.

Fig. 6 shows data for 100-300 ml. Freon-22 poured into discolored⁷ (through standing in open containers) and pure mineral oil⁵. It is seen that

(1) The data show considerable scatter, which seems to be typical of results obtained in vapor explosion measurements, where the rate of formation of new contact area seems to depend upon probabilistic quantities, such as turbulent pressure and velocity fluctuations, degree of initial mixing of the two fluids, and entrapment of one fluid inside the other.

(2) There is a considerable effect of impurities in the mineral oil on the probability of energetic interaction. Impure mineral oil data rise rapidly towards the maximum available pressure (vapor pressure of the volatile liquid at T_n) for $T_i \geq T_n$, where the interfacial temperature T_i is calculated from Eq. (3); and then decrease smoothly as $T_i \rightarrow T_{crit}$, the critical temperature of Freon-22. On the other hand, pure mineral oil shows a considerably lower rise rate, with the maximum pressure not being achieved, again falling off towards zero as $T_i \rightarrow T_{crit}$. It should be noted that intermediate-scale mixing data may not represent large-scale mixing effects, where one would expect the theoretical maximum pressure to be developed if energetic interaction occurs at all, simply because the random events are averaged over a much larger volume, and the inertial constraint requirements are satisfied. On the other hand, it is clear that the physical properties of the host liquid, including surface properties, play an important role, as was also indicated by the data shown in Figs. 1-4.

(3) Depending upon the choice of standard deviation, S , and mean, \bar{v} , for the probability distribution of random contacts, Eq. (17), one obtains predicted curves which form a fairly good envelope for all data, but follow the impure oil data more closely. In agreement with the data, there are no energetic interactions, with this mode of contacting, for $T_i < T_n$. The maximum pressure rises rapidly towards its theoretical value when T_i exceeds T_n , independent of choice of parameters. Parametric effects appear only after the peak is reached. If one assumes a broad distribution of random contacts ($S=2$), which physically seems to be likely, the resulting curves are quite insensitive to the mean value of the contact area, which is proportional to \bar{v} . It should be noted that these curves were calculated using the empirical correlation for the critical Weber number, Eq. (1), but using the physical properties of the oil, which forms the first splash, to determine We_2 . If We_1 had been used instead, quite similar curves are obtained, as shown in Fig. 7.

When mineral oil was poured into Freon-22, the same trends were observed (Fig. 7), although here the theoretical maximum pressure was attained with pure mineral oil whose temperature was 50°C above the

minimum for energetic interaction. For these data the model predictions are less satisfactory, and an alternative model will be discussed below.

Fig. 8 shows data for Freon-12 poured into impure mineral oil, with similar trends as in Fig. 6. Here the theoretical maximum pressure was not achieved, although there was a rapid rise in observed pressure as T_i exceeded T_n .

IV. Concluding Discussion

The propagation model presented here differs in some details from that of Henry and Fauske,⁵ although both are consistent with some peak pressure data obtained by Henry, et al.⁷ Clearly, additional experimental information is needed for further evaluation of these theories. Nevertheless, it should be emphasized that even at this time a number of important observations concerning the requirements for a vapor explosion can be made. Both theories postulate that spontaneous nucleation is a necessary requirement for vapor explosions. In the case of Freon-oil, which can be considered to be a "well-wetted" system, this implies homogeneous nucleation. For metal-water systems, however, vapor-free heterogeneous nucleation may take place, in view of the unique surface properties of water. Indeed, for aqueous systems it is difficult to suppress very small pre-existing surface nuclei. The practical effect, however, is the same in that nucleation may occur in metal-water systems at liquid-liquid interfacial temperatures somewhat below the homogeneous nucleation temperature of water, but with comparable time scales and

vapor pressures. Another important requirement common to both the splash and capture theories, as well as the Freon-oil data, is the necessity for film boiling to occur when the two liquids are initially mixed. This requirement is not satisfied by the sodium-UO₂ system, based on the Henry film boiling correlation. Rapid breakup therefore occurs as the two liquids are mixed, preventing a highly energetic interaction. Our current assessment, therefore, is that a sodium-UO₂ vapor explosion in a reactor environment is extremely unlikely.

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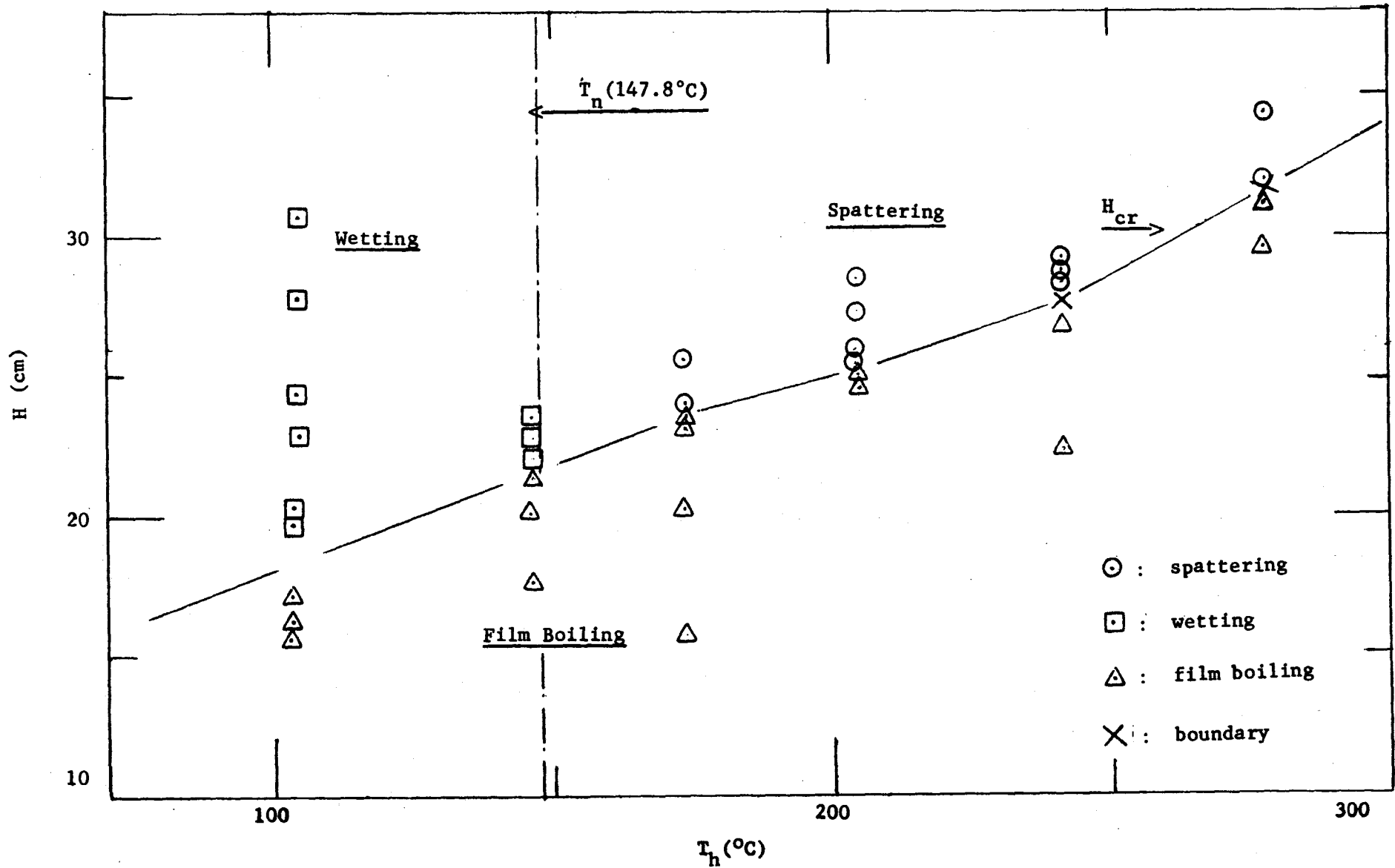


Fig. 1 Modes of Interactions with n-Pentane Droplets Impinging on a Hot Silicone Oil Surface. H = release height, $d = 0.143$

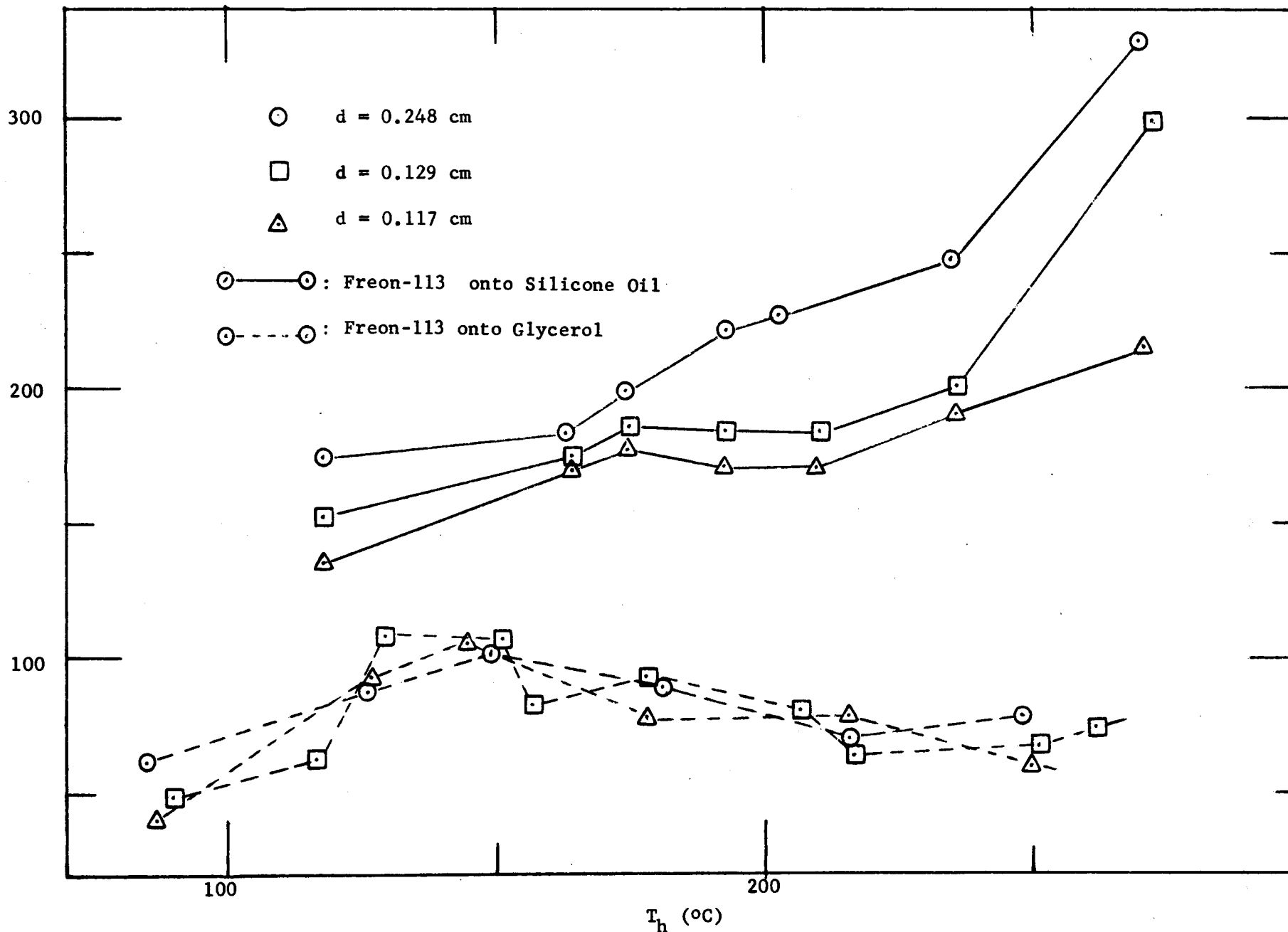


Fig. 2 Critical Weber Number of Freon-113 Droplets Impinging on Silicone Oil and Glycerol

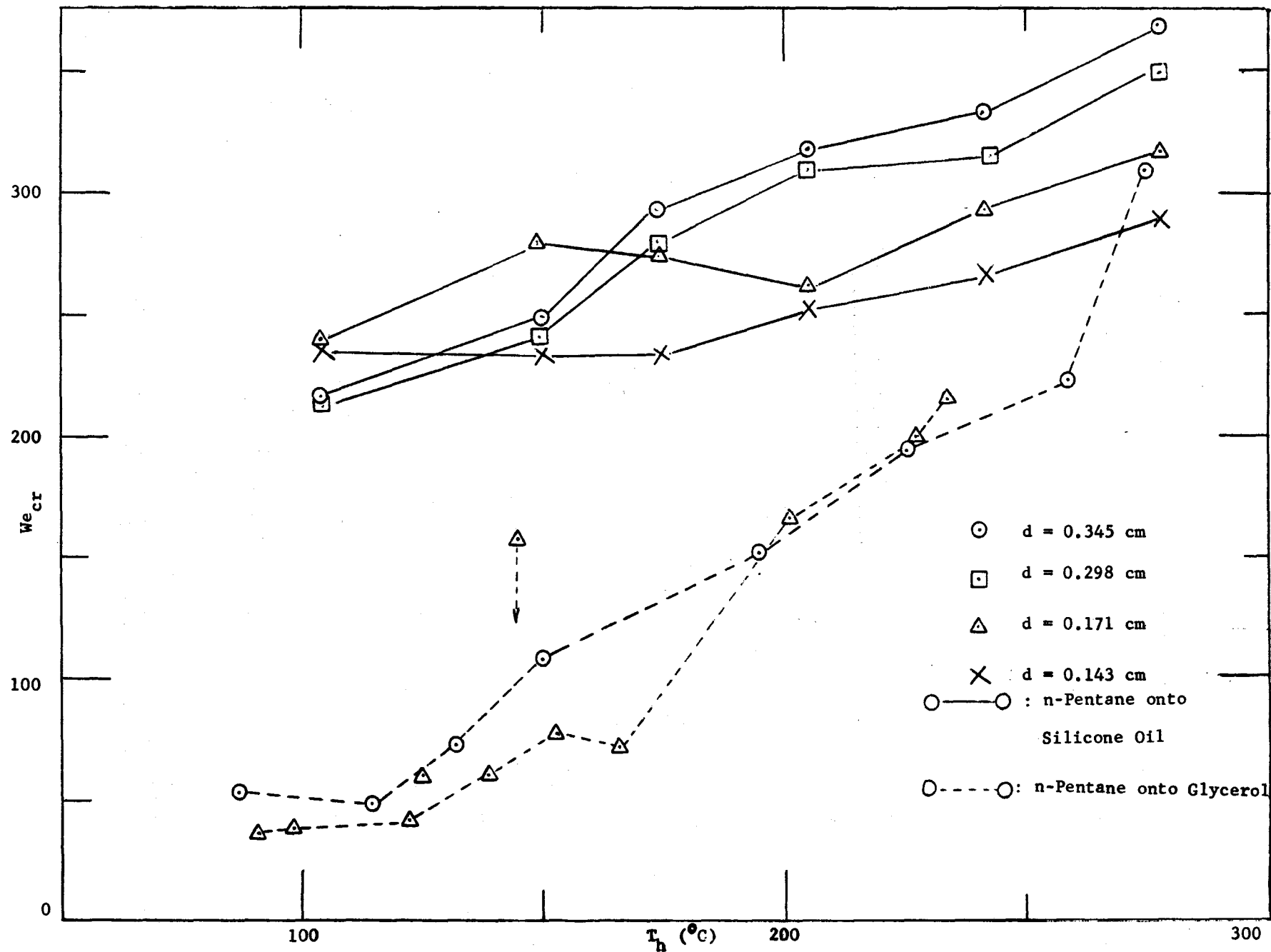


Fig. 3 Critical Weber Number of n-Pentane Droplets Impinging on Silicone Oil and Glycerol

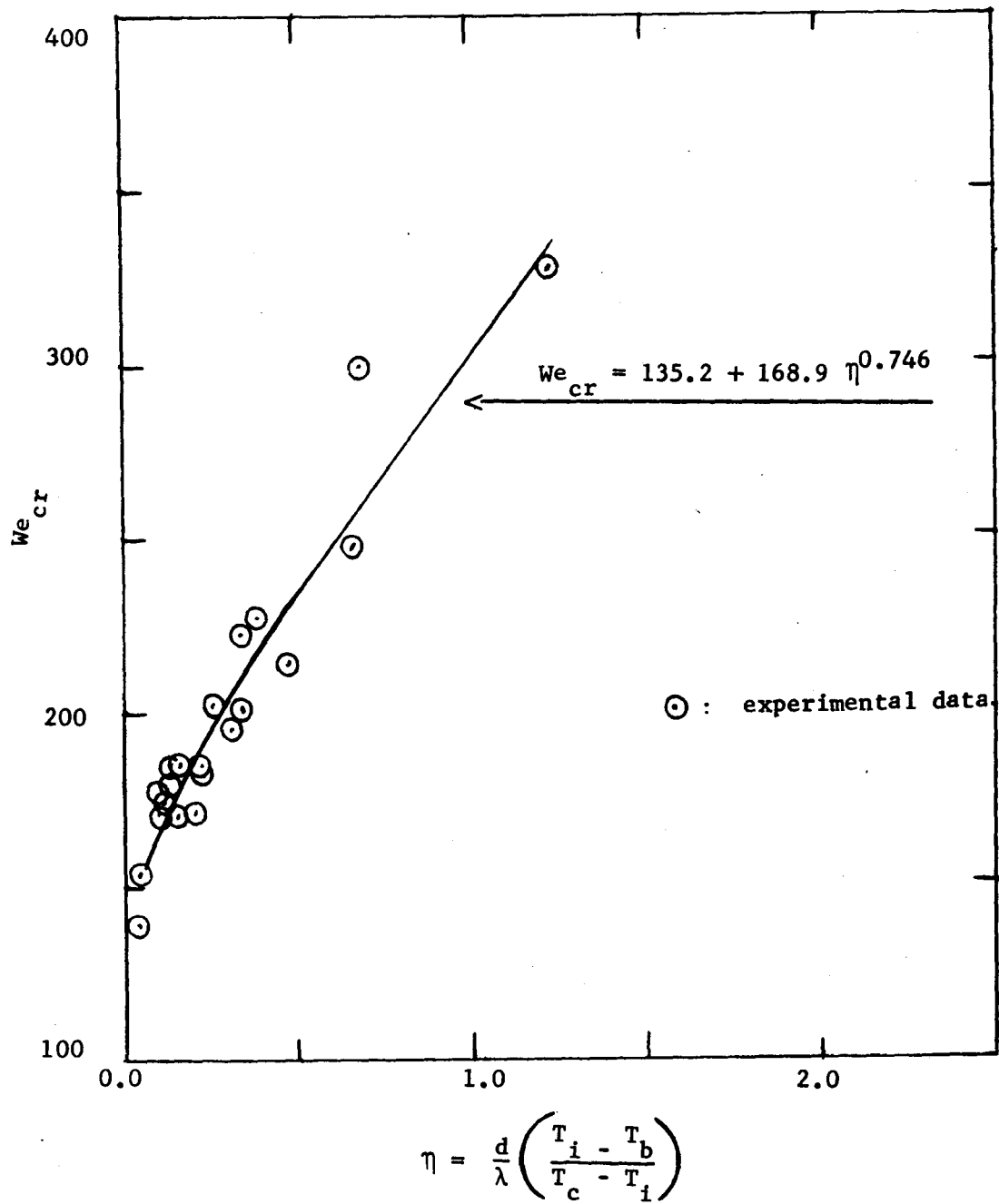


Fig. 4 Experimental Correlation of Critical Weber Number for Freon-113 Droplets Impinging on a Silicone Oil Surface

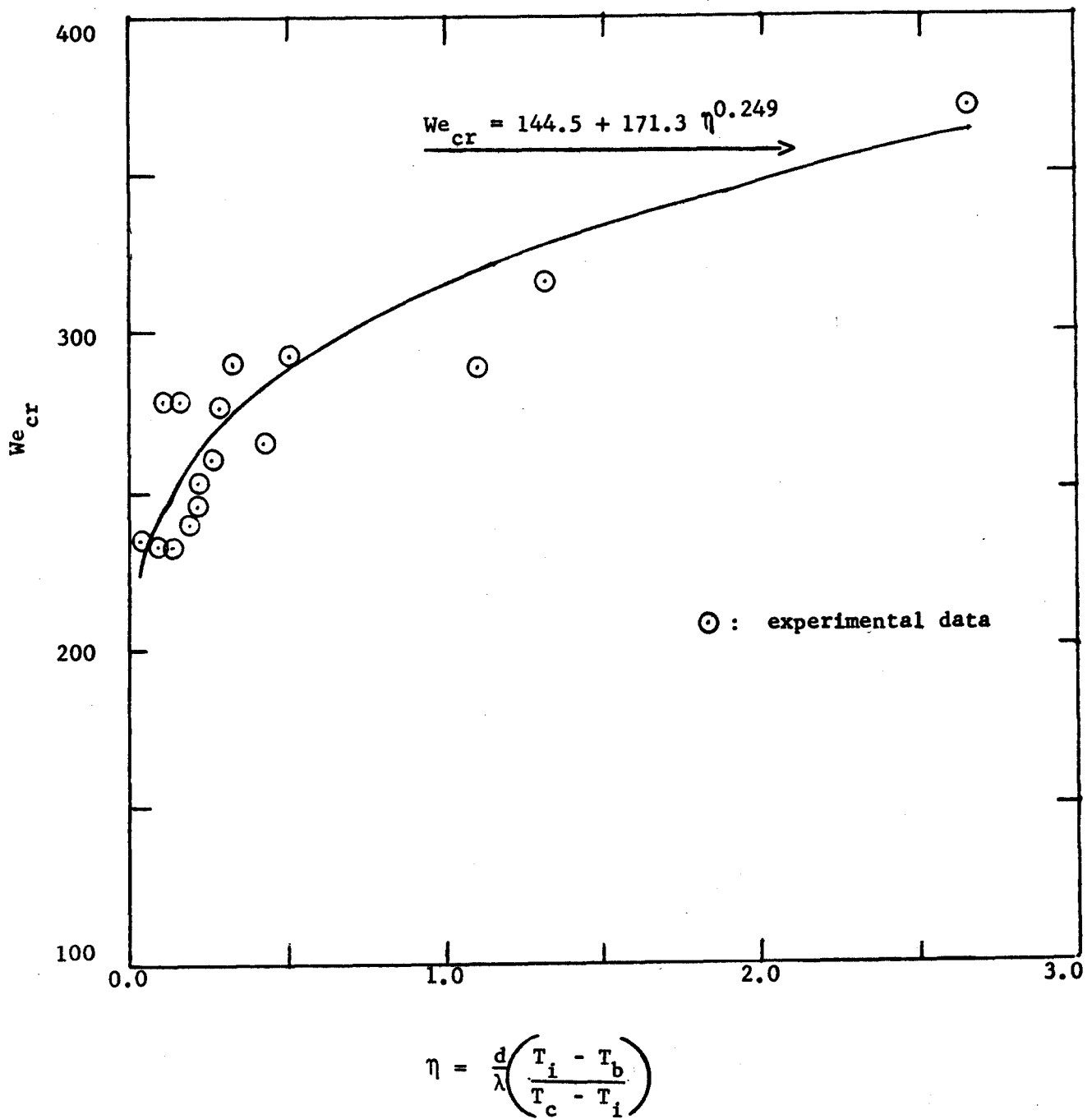


Fig. 5 Experimental Correlation of Critical Weber Number for n-Pentane Droplets Impinging on a Silicone Oil Surface

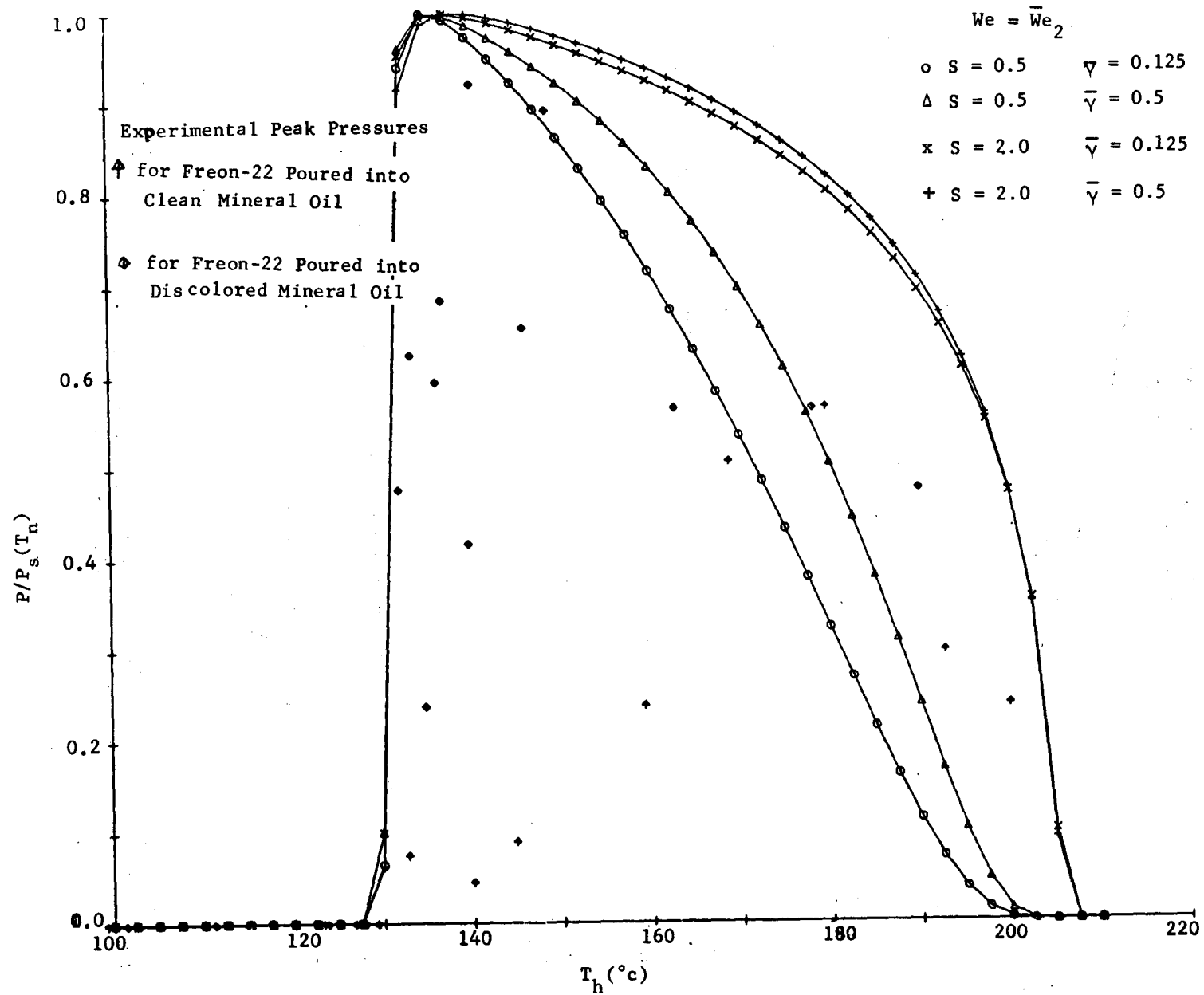


Fig. 6 Explosive Interaction Pressures for Freon-22 Poured into Mineral Oil

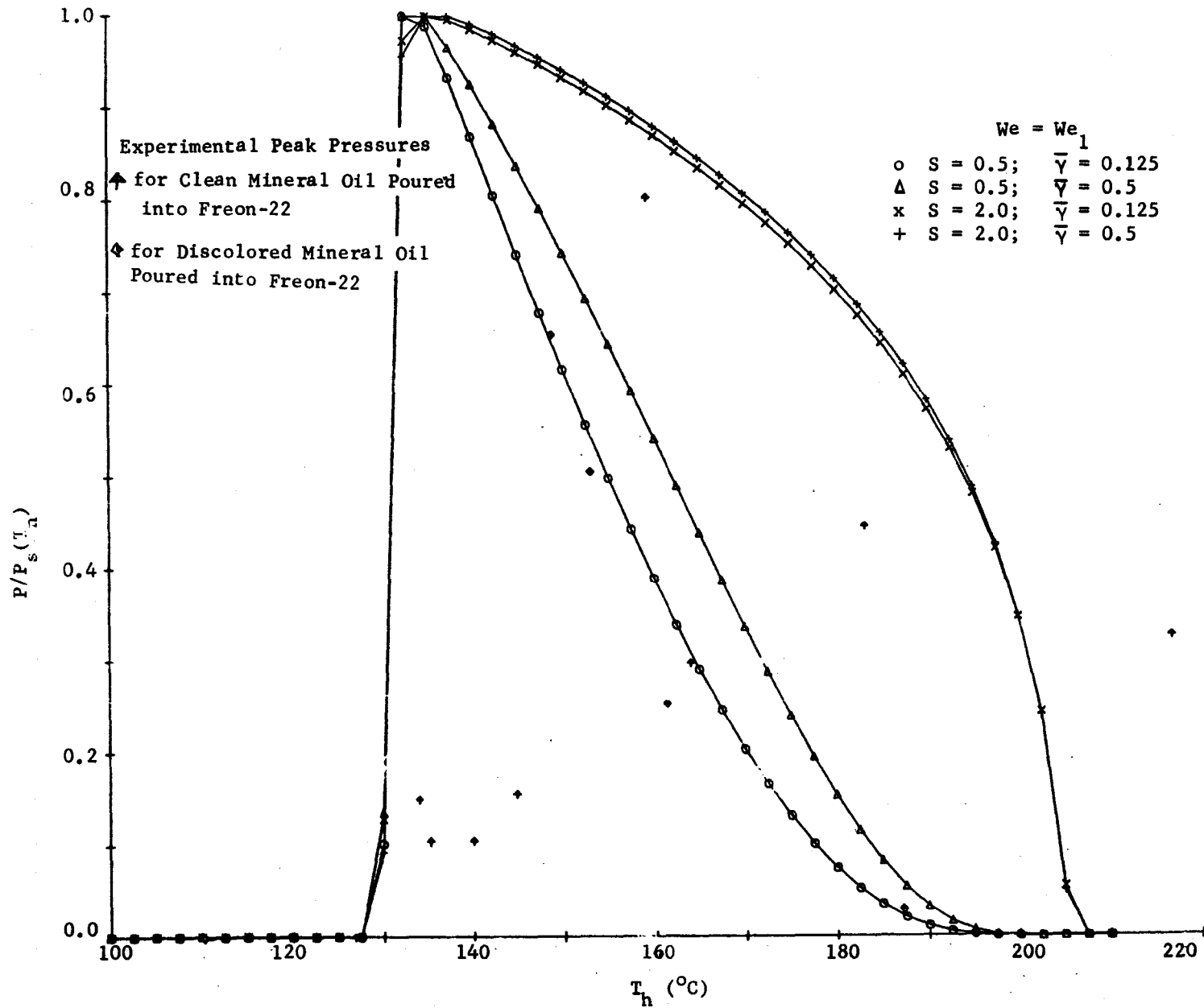


Fig. 7 Explosive Interaction Pressures for Mineral Oil Poured into Freon-22

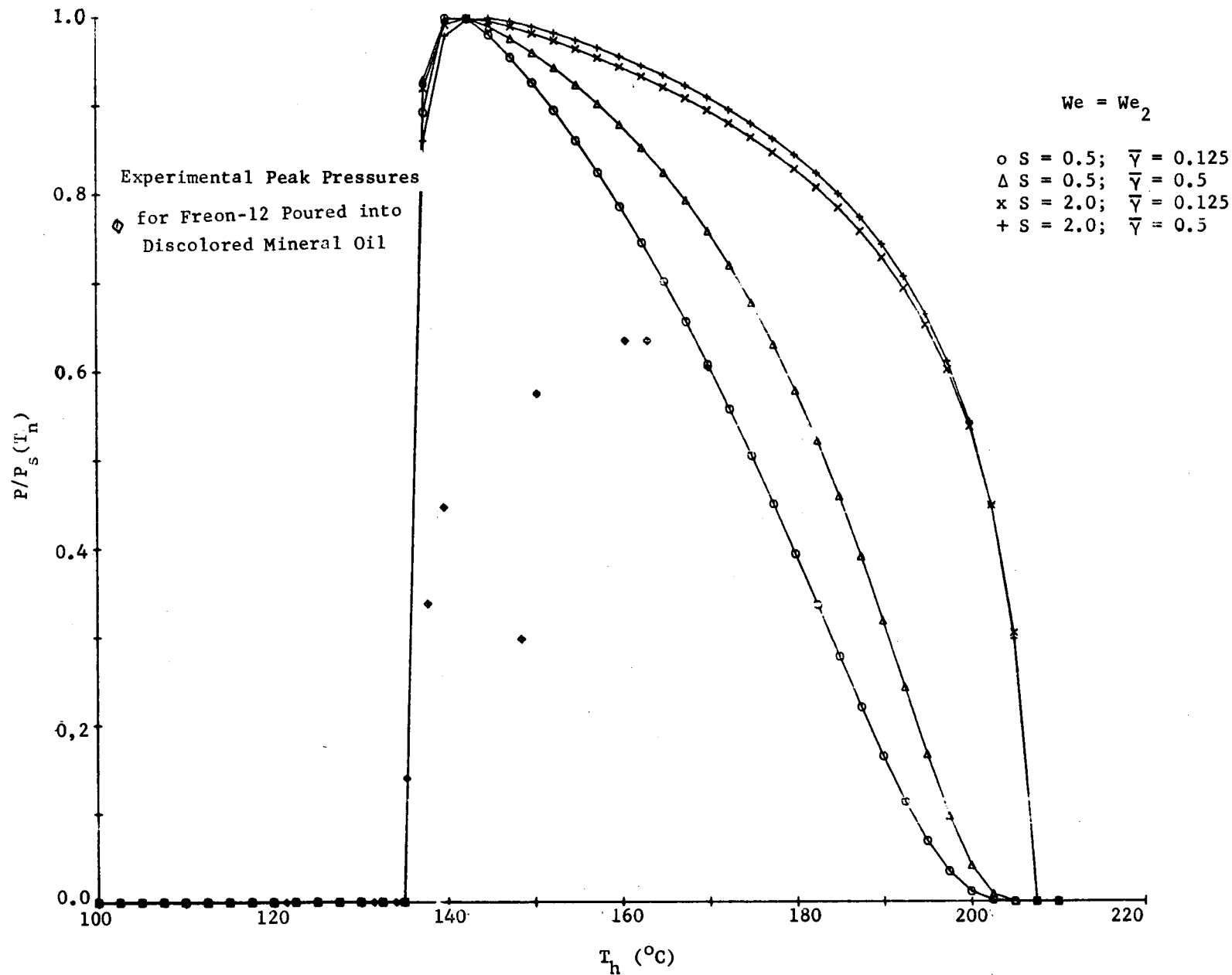


Fig. 8 Explosive Interaction Pressures for Freon-12 Poured into Mineral Oil