Research examining whether negative affect leads to drinking has produced mixed results (Greeley & Oei, 1999; Sher & Grekin, 2007). The current project enlisted participants (n=43) oversampled for affective instability, arguably making them at higher risk for negative affect-driven alcohol consumption. The goals of this study were to 1) validate an ambulatory device for measuring electrodermal activity (EDA) and to 2) examine the relations between emotion, EDA, and alcohol use in real-time. Multiple self-reports of emotion, alcohol use, and behavior were obtained from participants each day over the course of one week using electronic diaries. EDA was assessed continuously during waking hours. The results suggested that ambulatory measurement of EDA is feasible, and agreement between ambulatory measures and traditional laboratory measures was moderate to high for number of skin conductance responses per minute. Skin conductance level was less consistent across measures. With regard to ambulatory findings, high negative affect and high arousal states during the day were generally related to decreased likelihood of same-day drinking and decreased estimated blood alcohol concentration, while positive affect was related to increased likelihood of drinking. Hostility and number of skin conductance responses interacted, such that low hostility and low arousal was related to greater amounts of alcohol consumed. In sum, negative affect and arousal were related to alcohol use in real-time, but effects were small and both were generally protective against alcohol consumption at the day-level. This study helps to clarify the role of arousal in affect-related drinking, while also adding to accumulating evidence that suggests negative affect-related drinking may not be an immediate coping response. Positive-affect drinking may be most relevant in early stages of alcohol use, even in an emotionally dysregulated sample.